# Combining biosolids with carbonaceous materials to mitigate nitrogen-losses

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A thesis
submitted in partial fulfilment
of the requirements for the Degree of
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by
Dharini Paramashivam

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Biosolids are the solid by-product of wastewater treatment plants. Humanity produces some 50 kg/person/year, with global output exceeding 10 $\times 10^6$ t/year. Disposal of biosolids costs New Zealand (NZ) around $33 \times 10^6$ dollars/year. Most biosolids are either burned or placed in landfills, which is not a sustainable solution. Moreover, burning requires energy and results in greenhouse gas emissions. Biosolids are mostly organic matter and contain high concentrations of plant nutrients. Biosolids can also contain pathogens and contaminants, which is why they are not typically applied to NZ's high value soils. However, in NZ and elsewhere, biosolids are used to rebuild degraded soils for the production of non-food crops such as timber. Applying biosolids to soil improves plant growth, but may result in high levels of nitrate ($NO_3^-$) leaching and can introduce contaminants into the food chain. I aimed to determine the effect of mixing biosolids with carbonaceous materials (sawdust, biochars, and lignite) on $NO_3^-$ leaching from biosolids-amended soil. Sawdust/wood-waste was derived from *Pinus radiata* (D. Don), a common forestry species. Biochar was made by pyrolysis as *P. radiata*, waste at temperatures between 350°C and 550°C. Low-grade lignite coal, which is blended with high-grade coal for its disposal, was obtained from Solid Energy, NZ. The capacity of the amendments to sorb ammonium ($NH_4^+$) and $NO_3^-$ was measured using batch experiments. Solutions containing 100

mg/L of $NH_4^+$ or $NO_3^-$ were separately mixed with the amendments in 1:10 materials: solution ratio. Leaching of biosolids mixed with these amendments was determined using column leaching experiments. Columns (4 cm height × 4 cm diameter) containing biosolids mixed with biochars, lignite or sawdust in a 1:1 ratio were irrigated with 5 mL of deionised water and the resulting leachate was collected weekly. Large lysimeters (70 cm height × 50 cm diameter) were filled with intact columns of the Lismore Stony Silt Loam (low fertility soil). There were three replicates of the following treatments: control (no amendment), biosolids added at a rate equivalent to 400 kg N/ha, biosolids + lignite (1.5:1 by weight) and biosolids + biochar (1:1 by weight). All $NH_4^+$ and $NO_3^-$ concentrations were determined using Flow Injection Analysis (FIA). Batch experiments revealed that none of the amendments adsorbed significant amounts of $NO_3^-$. Biochar and lignite adsorbed significant amounts of $NH_4^+$, giving sorbed/solution $NH_4^+$ concentration quotients of up to 33 and 4.4 respectively. No nitrification occurred during this long-term sorption. The time to reach equilibrium of the lignite $NH_4^+$ mixture was in the order of 6 hr, while the biochar took some 150 hr to reach equilibrium. Increasing pyrolysis temperatures resulted in charcoals with an increased ability to sorb $NH_4^+$. Unpyrolyzed sawdust did not adsorb significant amounts of $NH_4^+$, however, sawdust almost eliminated $NH_4^+$-N leaching and reduced $NO_3^-$-N leaching by >40%. Low temperature biochar reduced $NH_4^+$-N leaching from the columns by 40 - 80%. Overall, dry sawdust and low temperature biochar are the potential carbonaceous materials to mitigate N leaching from biosolids.

***Keywords:*** *Biosolids, carbonaceous materials, biochar,lignite, lysimeter,leachate*

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# Chapter 1: General Introduction

## 1.1 Biosolids

Biosolids contain the solid fraction of sewage treatment. They usually contain significant amounts of water, with a dry matter content ranging from 15% to 96%, averaging 28% (Jones-Lepp & Stevens, 2007). Biosolids have high concentrations of organic matter (50 – 70%) and beneficial plant nutrients, such as nitrogen (N), phosphorous (P), potassium (K), calcium (Ca), magnesium (Mg) and sulphur (S) (Banegas et al., 2007; NZWWA, 2003). They can also contain elevated concentrations of trace elements, especially zinc (Zn), lead (Pb), cadmium (Cd) copper (Cu), iron (Fe), nickel (Ni), boron (B), molybdenum (Mo) and manganese (Mn) (Esteller et al., 2009). These trace elements may be beneficial or detrimental to both plants and soil. Biosolids may also contain traces of endocrine disrupting compounds and pathogens (Garrec et al., 2003; Jones-Lepp & Stevens, 2007). The chemical composition of biosolids depends on the effluent source and the treatment process. It is therefore highly variable. Nevertheless, Table 1.1 shows the chemical properties of "typical" fresh and aged (stockpiled) biosolids. There is no clear cut definition for aged biosolids, but according to Bernal et al. (1998), the major differences were that fresh biosolids contain a high proportion of their inorganic N as ammonium-N ($NH_4^+$-N), whereas aged/matured biosolids contain a higher proportion of nitrate-N ($NO_3^-$-N).

Table 1.1. Physicochemical characteristics of typical fresh biosolids and aged biosolids [adopted from: (Bernal et al., 1998; Esteller et al., 2009; Knowles et al., 2011; Rigby & Smith, 2013)]. Concentrations are on a dry weight basis.

| | Fresh biosolids | Aged biosolids |
|---|---|---|
| Moisture content (%) | 83 | 53 |
| EC (mS/cm) | 5.2 | 8.3 |
| pH ($H_2O$) | 6.4 | 4.1 |
| Total C (%) | 45 | 28 |
| Organic matter (%) | 62 | 60 |
| Total N (%) | 4.3 | 2.7 |
| $NH_4$-N (mg/kg) | 3400 | 182 |
| $NO_3^-$ -N (mg/kg) | 5.1 | 4192 |
| C:N ratio | 8.4 | 6.9 |
| Olsen – P (mg/kg) | 5192 | 4683 |
| CEC (cmol/ kg) | 39 | 41 |
| $Na^+$( mg/kg) | 460 | 713 |
| $K^+$ (mg/kg) | 5183 | 4984 |
| $Ca^{2+}$ (mg/kg ) | 4268 | 9818 |
| $Mg^{2+}$ (mg/kg) | 3949 | 2204 |
| $Cu^{2+}$ (mg/kg) | 352 | 561 |
| $Cd^{2+}$ (mg/kg) | 32 | 2.8 |
| $Zn^{2+}$ (mg/kg) | 809 | 878 |
| $Pb^{2+}$ (mg/kg) | 79 | 112 |

### 1.1.1 Biosolids production: a growing environmental issue

Humanity produces some 27 kg of dry biosolids (sewage sludge) per person per year (Hue, 2014), with the world production exceeding $30\times10^6$ t/year (Ronald et al., 2008). This is expected to increase as the population grows and becomes more urbanised, leading to increased volumes of treated human waste. The total biosolids production of New Zealand is approximately 400,000 – 500,000 t/year (ANZBP, 2014). Global Water Intelligence (GWI, 2015) reported that China, the most populous country, has doubled its biosolids production from 2005 to 2015 (Figure 1-1).

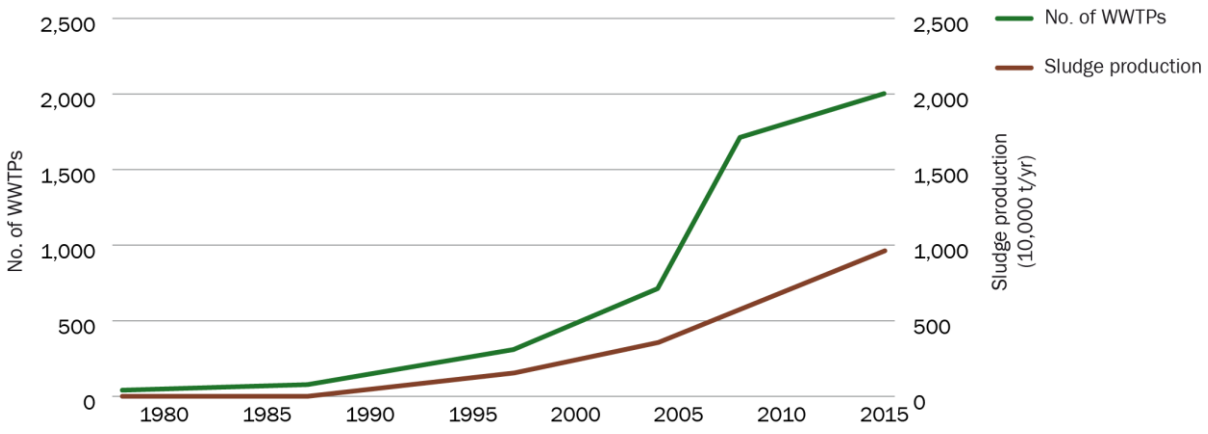


Figure 1-1. Graph showing sludge production in China, 1980-2015. (GWI, 2015) URL http://www.globalwaterintel.com/market-intelligence-reports/sludge-management/

### 1.1.2 Biosolids disposal

Disposal of biosolids is a global environmental issue. Worldwide, biosolids are disposed of into landfills and oceans (Ronald et al., 2008). They are also burned, with the resultant ash applied to land or disposed of in landfills (Ronald et al., 2008). In New Zealand, biosolids are disposed of through landfilling (60%), ocean discharge (10%), applied to agricultural land (10%), used for land rehabilitation (10%), composting (5%) or applied to forests (5%) (ANZBP, 2014). Land filling is expensive. In New Zealand, the cost is approximately NZ$200-250 per tonne, excluding transport costs, with an average annual cost of NZ$ $33\times10^6$ per year (WCC, 2008). Moreover, apart from the cost of landfilling biosolids, this methodology results in a waste of valuable plant nutrients and organic carbon (Table 1.1).

### 1.1.3 Land application

Biosolids can improve soil fertility when applied to land (Sanchez-Monedero et al., 2004). The proportion of produced and subsequently applied biosolids to land varies between countries. In the USA 63% of biosolids are applied to land (PIB, 2015), while in New Zealand 10% of biosolids are land-applied.

Biosolids contain pathogens and some trace metals, which can potentially endanger human health and soil quality (Singh & Agrawal, 2008; Sullivan et al., 2006). Therefore, there can be public opposition to the application of biosolids to prime agricultural land in NZ (Barnett & Russell, 2001). The risk of biosolids degrading soil quality is higher when repeated applications are applied and soil quality may decline due to the accumulation of Cd, Cu and Zn in concentrations that negatively affect soil microbial functions (Henry et al. (1994). Pre-treatment of biosolids can reduce the risk of land application of biosolids. For example, Bernal et al. (1998) showed that composted sewage sludge had significantly lower pathogen loads.

### 1.1.4 Rebuilding degraded soils using biosolids

An alternative to land application of biosolids is to use them for rebuilding degraded soils (Kowaljow et al., 2010). Here, the contaminants that they contain are less likely to enter food chains, especially if the land is rehabilitated into non-agricultural production such as forestry (Magesan & Wang, 2003; Wang et al., 2010). For example, the Christchurch City Council (CCC) is collaborating with Solid Energy New Zealand to reuse biosolids produced at the Christchurch Wastewater Treatment Plant (WTP) to rehabilitate mined areas at the Stockton mine site. Figure 1-2 shows the effect of applying biosolids (the green patches) with respect to improving vegetation on the mine site, compared to un-amended bare areas.

Figure 1-2. Outcome of biosolids application at the Stockton mine site (CCC, 2011).

In 2010, New Zealand had $2.5\times10^6$ ha of land in forestry. Radiata pine (*Pinus radiata* D. Don) plantations account for the vast majority of commercial plantings (Figure 1-3), of which several thousands of hectares are classified as degraded after logging (MAF, 2010). During logging, much of the top soil (which has a higher organic matter content) is removed. Moreover, soils under pine forests become acidic and depleted in plant nutrients (Eckehard et al., 2005). Similarly, lands affected by mining often fail to develop a vegetation cover and require remediation. Thus, there is potential to improve forestry soils via land application of biosolids.

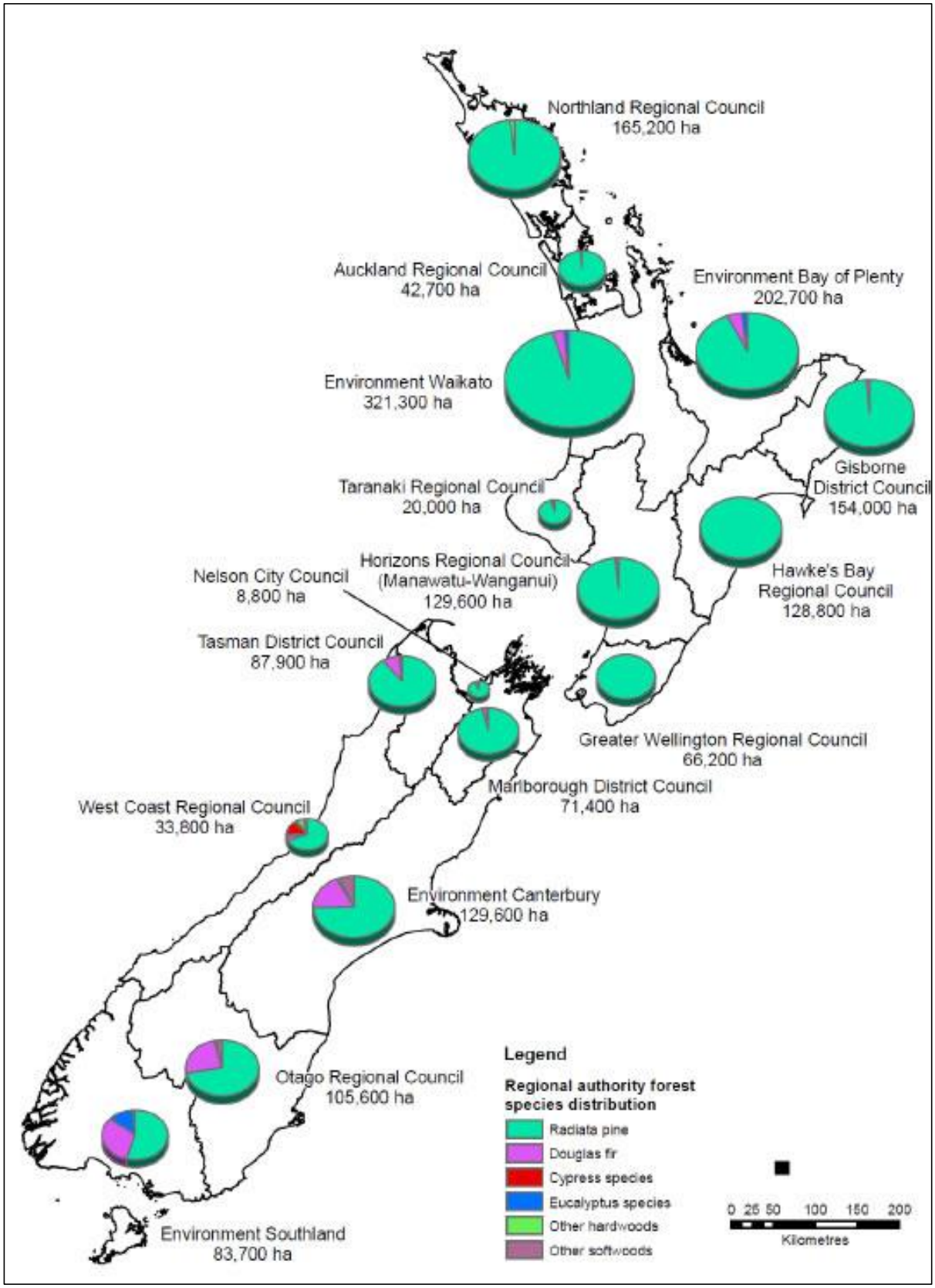


Figure 1-3. Distribution of commercial forest species by region in New Zealand (MAF, 2010).

Biosolids have been shown to successfully improve soils degraded through mining and forestry activities (Lee et al., 2003; Novak et al., 2009). Rebuilding such soils using biosolids has required high rates of application (50 – 400 t/ha) to achieve a meaningful increase in soil carbon and plant nutrients (Magesan & Wang, 2003). Given that biosolids comprise 2 – 5% N by weight (Lee et al., 2001), rebuilding degraded soil can result in excessive N loadings of 2500 - 20,000 kg/ha (Henry et al., 1994; Lee et al., 2001) which is well in excess of the maximum permitted N applications in most jurisdictions (ca. 200 kg N/ha/year). Excessive loading of mineral N is associated with high levels of $NO_3^-$ leaching (Davis, 2014). Korboulewsky et al. (2002) reported that rates as low as 30 t/ha could cause excess $NO_3^-$ leaching from a stony vineyard soil in France, while Samaras et al. (2008) reported that 10 t/ha was a safe application rate for biosolids with respect to $NO_3^-$ leaching. Others reported that biosolids application should not exceed 30 t/ha to control $NO_3^-$ leaching (Binder et al., 2002; Brenton et al., 2007; Lavado, 2006; Nash et al., 2011; Rajendram et al., 2011).

### 1.1.5 Mitigation of nitrate leaching from biosolids

More than 95% of N in biosolids is organic N, with smaller amounts of $NH_4^+$ and $NO_3^-$ (Correa et al., 2006). The ratio of $NH_4^+$ to $NO_3^-$ decreases as the biosolids age (Smith et al., 1998). When biosolids are applied to soil, the $NO_3^-$ present can leach immediately, often resulting in a flush of leaching (Knowles et al., 2011). Over time, the organic N mineralizes to $NH_4^+$, which is then nitrified to $NO_3^-$ (Figure 1-4). Reducing the amount of $NO_3^-$ leaching from biosolids requires that the N is held in the soil so that it can be taken up by plants rather than leached. Theoretically, this could be achieved at several stages in the leaching process (Figure 1-4). Plants will take up some of the $NO_3^-$ formed through nitrification, while the excess will either leach or undergo denitrification. Leaching occurs because negatively charged $NO_3^-$ ions are repelled from soil colloids that also generally carry a negative surface charge. Leached $NO_3^-$ will end up in either surface or ground waters. This results in reduced water quality, algal

blooms, and eutrophication (affecting flora and fauna) (Timothy et al., 2015). High concentrations of $NO_3^-$ in drinking water are harmful to human health (Andrews et al., 2007; Di & Cameron, 2002a; Goulding et al., 2008). Research by McKinney et al., (1999) indicated that high $NO_3^-$ levels in drinking water may cause stomach cancer and diabetes mellitus, but this remains unproven. The allowed maximum limit of $NO_3^-$ in drinking water is 10 – 11.3 mg $NO_3^-$-N/ L (WHO, 1984).

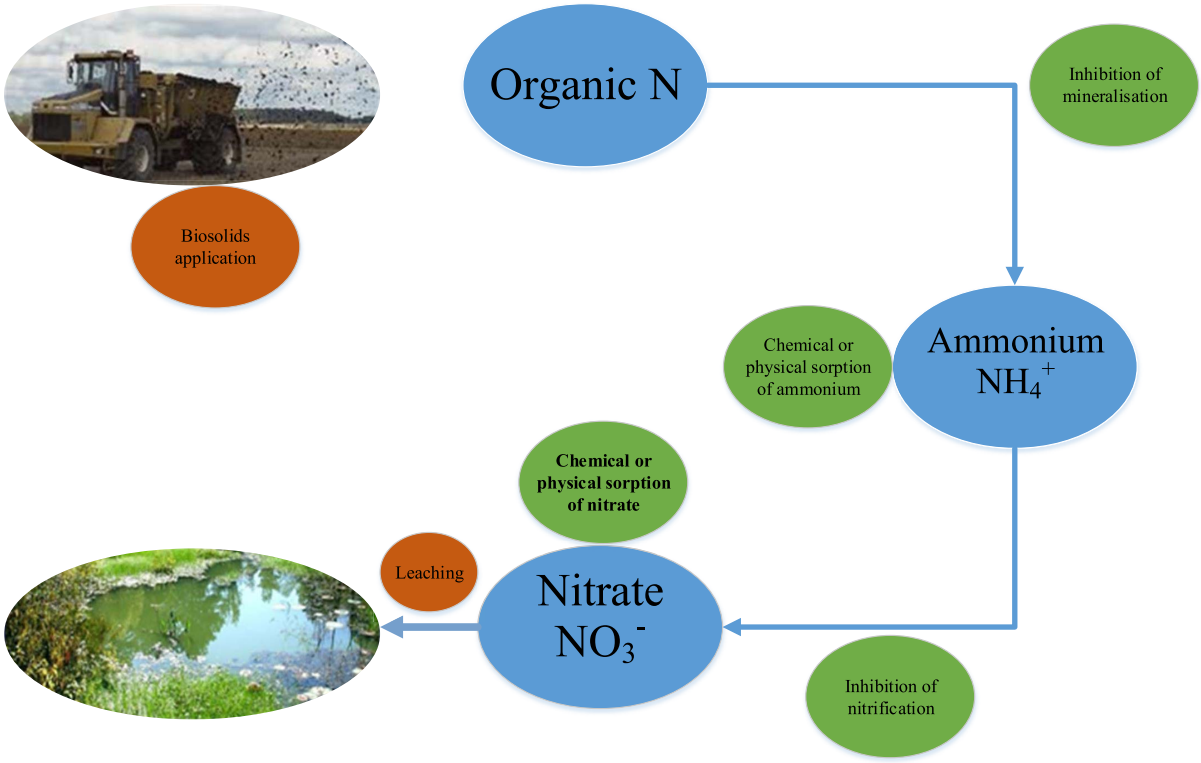


Figure 1-4. Nitrate leaching pathway from biosolids (shown in blue) and where potential changes could be made to reduce nitrate leaching (green).

The hypothesis for the research in this thesis is that mixing biosolids with carbon-rich materials could reduce $NO_3^-$ leaching from biosolids. Carbonaceous substances such as sawdust, biochar and waste coal (lignite), could be mixed with the biosolids, to offset some of the negative environmental effects of biosolids addition to soils (Knowles et al., 2011; Lee et al., 2001; Schmidt et al., 2001; Simmler et al., 2013). Composting biosolids with sawdust has been shown to effectively reduce $NO_3^-$ leaching (Tarek et al., 2012). New Zealand's timber industry produces large volumes of wood-waste, including sawdust, which is often

inappropriately disposed of in wood-waste piles (Robinson, 2007). Provided the sawdust is not contaminated with timber treatment chemicals such as copper (Cu), chromium (Cr) and arsenic (As) (CCA), this waste material may potentially be used to improve environmental outcomes from biosolids-amended soils. Costs would be greatly reduced if sawdust from the degraded land could be incorporated with the biosolids on site, rather than being composted beforehand. However, it is unclear whether un-composted mixtures would still be effective in mitigating $NO_3^-$ leaching. General properties of each of these materials are given in Chapter 4.

## 1.2 Sawdust/wood-waste

Figure 1-5. *Left*: Accumulated sawdust pile from a pine forest site in New Zealand: *Right*: Kopu sawdust timber waste pile (arrow) located in the North Island of New Zealand; an aerial view (Robinson et al., 2007).

Sawdust is a waste by-product of the timber industry. Timber processing on site includes the removal of bark and branches resulting in considerable amounts of sawdust accumulating over time (Figure 1-5 *Left*). Robinson et al. (2007) studied a timber waste pile (located on the Coromandel Peninsula, North Island, New Zealand (37.2°S, 175.6°E) which accumulated over a 30 yr period, eventually covering an area of approximately 3.6 ha and to a depth of 15 m (Figure 1-5 *Right*). The leaching of concentrated tannins, contained in wood-

waste piles, can cause contamination of ground and surface waters. Similarly, Wendong et al. (2005) showed that the tannins leached from wood-waste depleted soil oxygen.

Sawdust waste, as a carbon-rich material, can be directly mixed with biosolids to reduce $NO_3^-$ leaching. Alternatively, sawdust can be converted to biochar. There is a dearth of research examining the effectiveness of mixing sawdust with biosolids. Lee et al. (2001) applied biosolids mixed at different rates with sawdust, to two soil types and grew corn (*Zea mays*), wheat (*Triticum aestivam* and soybeans (*Glycine max*) over three growing seasons. Sawdust reduced $NO_3^-$ leaching from the biosolids-amended soil by 16.4%, but also negated the positive effects of adding biosolids on plant growth.

Tarek et al. (2012) studied the composting of sewage sludge, sawdust, and organic waste from the food industry. They concluded that both fine sawdust and organic waste mixed with sludge were the most effective as compost with respect to plant growth. There was no effect on inorganic-N leaching when Bugbee (1999) mixed hardwood dried sawdust in potting media containing biosolids compost. All the leaching occurred during the first four weeks of the 5-month experiment, and mostly in the form of $NH_4^+$-N. Bugbee (1999) found no difference in the growth of *Coreopsis grandiflora* L. and *Rudbeckia hirta* L. ("Goldstrum") plants when rates of sawdust addition were increased.

Banegas et al. (2007) composted either aerobic or anaerobic sewage sludges with sawdust. Two ratios of sludge to sawdust 1:1 and 1:3 (v/v) were used and *Lepidium sativum* seeds were germinated. The 1:3 ratio appeared to reduce toxic effects (including some phytotoxic compounds) of the anaerobic sludge composting mixture, but the 1:1 ratio was sufficient for composting and agricultural use of aerobic sludge.

Keränen et al. (2015) used a chemically modified sawdust with increased surface functional groups (*Pinus sylvestris*) to sorb $NO_3^-$. They treated pine sawdust with epichlorohydrin, ethylenediamine and triethylamine in the presence of N,N-

dimethylformamide and achieved sorption capacities of 22.2-32.8 mg/g for $NO_3^-$-N. However, in this current study sawdust will be used with no modification.

Harmayani and Anwar (2012) showed that dried *P. radiata* (pine) sawdust could adsorb nutrients ($NH_3$-N, $NO_3$-N and $NO_2$-N) from storm water. They showed sawdust sorbed or immobilized 55% of $NH_3$-N and 100% of both $NO_3^-$-N, and $NO_2$-N. Kim et al. (2003) showed that alfalfa, leaf mulch compost, newspaper, sawdust, wheat straw, wood chips, and elemental sulphur, could potentially be used to remove contaminants from storm water.

Xuan et al. (2010) used a green sorption medium (comprising recycled materials) to remove all pollutants from the underground field drain of a sewage treatment and disposal system. An increase in denitrification was achieved with less than 10% sawdust in their adsorption method. In anaerobic conditions, sawdust acts as an electron donor that completely reduces any introduced $NO_3^-$ to $N_2$ gas via denitrification. These authors also showed that 96% of $NO_3^-$ was removed when 24 hr of contact (green sorption medium and ground water) was followed by 24 hr of anaerobic conditions.

There is limited literature explaining the exact mechanisms by which sawdust adsorbs contaminants from storm water and other sources. Shukla et al. (2002) showed that sawdust can adsorb dyes, oil, toxic salts and a variety of cations, including heavy metals, from water. Different types of sawdust and their sorption ability were shown to be pH dependent, and this provides a possible mechanism for the sorption by sawdust. Shukla et al. (2002) theorized that the sawdust sorption mechanism included (i) ion-exchange and hydrogen bonding in sawdust, as well as (ii) compounds in the cell walls, such as lignin, cellulose and hydroxyl groups that act as an ion-exchange media. This would explain the results reported by Bugbee (1999) where he found no significant reduction in N leaching when he used sawdust from hardwood, which contains less lignin than softwood, 18 – 25% and 25 -35% respectively (Shukla et al., 2002).

The sawdust contact time and the concentration of the sorbent medium affects the sorption efficiency. Using sorption agitation periods between 21 hr and 96 hr, Harmayani and Anwar (2012) showed 21 hr was effective on $NO_3^-$-N sorption at 0.5 mg/L concentration. Generally, most research uses 20 min (Wahab et al., 2010) or 2 hr to 6 hr (Shukla et al., 2002).

The C:N ratio of an organic material influences N immobilization (McLaren & Cameron, 1996). When organic matter decomposes in soil, there is a relative increase in the inorganic N content. This process affects the C:N ratio. Mineralization (*Equation 1.1*) is a result of excess N presence and vice versa. The threshold for net mineralization of organic matter is a C:N ratio of less than 25:1.

$R\text{-}NH_2$ (in organic matter) + $H_2O \rightarrow NH_3$ + R-OH + energy [Equation 1.1]

Equation 1.1 is called mineralization (McLaren & Cameron, 1996).

According to Suzuki et al. (1974), nitrification by Ammonia Oxidising Bacteria (AOB e.g. *Nitrosomonas* sp.) involves two reactions (*Equation 1.2 and 1.3*). Nitrification transforms ammonia ($NH_3$) to nitrite/nitrous acid ($HNO_2$). A similar situation exists in *Nitrobacter* sp. bacteria, where they use $HNO_2$, rather than $NO_2^-$, to form $NO_3^-$ (Suzuki et al., 1974).

$NH_3 + O_2 + 2H^+ \rightarrow NH_2OH + H_2O$ [Equation 1.2]

$NH_2OH + H_2O \rightarrow HONO + 4H^+$ [Equation 1.3]

Where organic matter has less N (a high C:N ratio) microbes immobilize inorganic-N in the soil. In this case, they will take up any mineral N available from their surrounding environment. This process is called immobilization.

The C:N ratio is one of the most important factors governing the composting of organic waste (Huang et al., 2004; Ogunwande et al., 2008). Ogunwande et al. (2008) reported that the composting efficency of chicken manure and sawdust was optimal at a C:N ratio of 25:1, with

minimal loss of total N. Tarek et al. (2012) measured the effect of initial C:N ratios of 30:1 and 20:1 when composting sawdust with sewage sludge. They reported that only an initial C:N ratio of 30:1 was suitable for composting.

## 1.3 Biochar

Biochar is a by-product obtained following the pyrolysis of biomass (Kloss et al., 2012). The pyrolyzing process is controlled by a range of parameters, such as feedstock type, pyrolyzing temperature, activation conditions, and the supply of oxygen. Each of these parameters influences the characteristics of a particular biochar (Figure 1-6).

Biochar can be used as a soil conditioner to improve a soil's physical properties (e.g. soil texture, aeration, water holding capacity and microbial habitat), and chemical properties (e.g. pH, conductivity, Cation Exchange Capacity (CEC)). It has been advocated as one of many partial solutions to mitigate human-induced climate change (Woolf et al., 2010). When untreated biomass is added to a soil, natural decomposition leads to greenhouse gas emissions (Gholz et al., 2000). Therefore, converting this biomass to biochar can increase soil fertility and offset greenhouse gas emissions that would otherwise occur via decomposition.

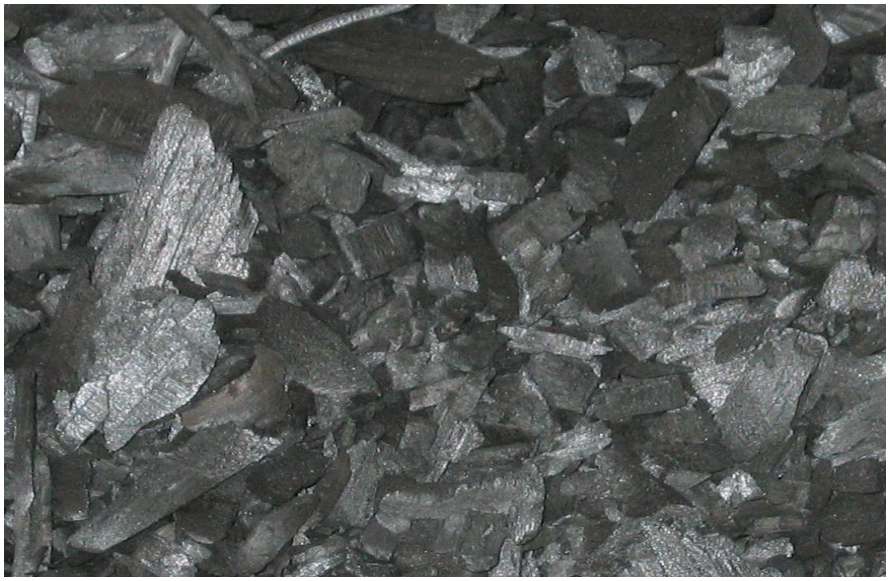

Figure 1-6. Biochar pyrolyzed from pine wood-waste (Photograph by Dharini Paramashivam, 2011).

Previous studies have shown that biochar pyrolyzed at temperatures >700ºC had the ability to sorb inorganic N from various sources via surface functional groups (Lehmann, 2007). Kameyama et al. (2012) showed that bamboo charcoal manufactured at 800ºC leached just 5% less $NO_3^-$ from an amended soil, whereas a char produced at 400ºC had no effect on $NO_3^-$ leaching.

A single study demonstrated that under certain conditions, biochar could reduce $NO_3^-$ leaching by over 50% when a pasture soil was amended with biosolids, but the authors did not determine any mechanism for this reduction (Knowles et al., 2011). The biochar was made from Monterrey Pine (*P. radiata*) pyrolyzed at 350ºC. It is unclear which biochar properties were responsible for the $NO_3^-$ leaching mitigation reported by Knowles et al. (2011). Identifying these properties would allow biochars to be specifically designed for mitigation of $NO_3^-$ leaching from biosolids-amended soil.

The sorptive properties of biochar are profoundly affected by the source material/feed stock (Enders et al., 2012), the pyrolysis temperature (Asada et al., 2002; Glaser et al., 2002; Lehmann, 2007), the particle size (Kwapinski et al., 2010) and the weathering of the material in soil (Novak et al., 2009). Cheng et al. (2006) studied the oxidation process of black carbon

at 30°C and 70°C, in biotic and abiotic conditions over a 4-month period. The rate of oxidation was higher under abiotic conditions at 70°C, where CEC increased 53 - 538% (due to an increase in the carboxylic functional group). Biochar weathered in soil showed higher $NH_4^+$ sorption than freshly pyrolyzed biochar. Moso bamboo (*Phyllostachys pubescens*) biochar pyrolyzed at 500°C adsorbed more $NH_3$ (from initial 100 mg/L to 5 mg/L) than biochars pyrolyzed at > 700°C (from 100 mg/L to 60 mg/L) in 3 hr (Asada et al. (2002). Asada et al. (2002) reasoned that pyrolyzation at higher temperatures removed the aromatic acid functional groups. Different groups would be removed at specific temperatures and they concluded that biochar must be specifically selected for use as an adsorbent.

Wildfire is an event that naturally adds charcoal to soil. Comparing pine forests that had undergone a minimum of 2-3 fires in the last 100 yr with a forest that had suffered no recent fire showed that the fires resulted in high soil charcoal contents, which resulted in higher rates of nitrification (Ball et al., 2010; Berglund et al., 2004; DeLuca & Sala, 2006).

A question often posed is what is the adequate and cost effective rate of biochar application? As yet, no set rate of biochar land application has been defined, with studies using different rates. Depending on their needs, the cost of biochar manufacture, transport and application, can be restricting factors. A few examples are 15 t/ha biochar (Mukherjee et al., 2014), 20 t/ha biochar (Clough et al., 2010), 22.4 t/ha biochar (Lentz et al., 2014), 25 t/ha biochar (Scharenbroch et al., 2013) and 102 t/ha biochar (Knowles et al., 2011).

### 1.3.1 Possible mechanisms involved in N retention by biochar

(i) Adsorption of $NH_3$/ organic-N due to the cation exchange reaction (Mandal et al., 2016; Taghizadeh-Toosi et al., 2012a; Thangarajan et al., 2015).

(ii) Increase in immobilization of N due to high labile carbon availability in biochars. Ippolito et al. (2012) showed that low temperature charcoal (250°C) leached less $NO_3^-$ compared to the

ones produced at 550ºC. They reasoned that the presence of available C/ degradable C in low temperature biochar immobilized the N, hence $NO_3^-$ leaching was reduced.

(iii) High temperature pyrolyzed biochar appears to adsorb $NO_3^-$ due to the increase in surface area and N-containing functional groups of biochars (Kameyama et al., 2012; Mizuta et al., 2004; Yao et al., 2012).

(iv) The water holding capacity of the biochar reduces the rate of leaching through the biochar (Dempster et al., 2012b; Lehmann et al., 2003). Here the soil type and particle size of the char and pore size distribution are key to reduce leaching.

(v) Better crop cover/yield due to biochar-amendment, where more N/nutrient uptake by pasture leads to a reduction in leaching (Knowles et al., 2011).

## 1.4 Lignite

Lignite is abundant worldwide: the proved and recoverable world lignite resources, cited by the WEC (2010) are ca. $195\times10^9$ t, with $333\times10^6$ t being located in New Zealand (Figure 1-7 *Left*). It is considered a low-grade coal (always blended with high-grade coal) because of its high moisture content, which requires more energy to produce heat, and higher sulphur content, which forms acid rain. Burning this lignite (Figure 1-7 *Right*) would contribute ca $8\times10^9$ t of $CO_2$ (CANA, 2012) to the atmosphere, and any alternative use would reduce this $CO_2$ burden.

Lignite has a similar structure to many biochars (Kwiatkowska et al., 2008). However, there are also important differences. Whereas a hypothetical biochar comprises 54.9% C, 2.14% H, 4.97% N and 20.04% O (Ozcimen & Karaosmanoglu, 2004), a typical elemental composition of lignite is 70% C, 8 - 5% H, 1.2 % N and 25% O (Kwiatkowska et al., 2008). In general, lignite has a greater number of functional groups than biochar. This results in a higher CEC in lignite, typically 20 -70 $cmol_c/kg$ (Wong et al., 1996), compared to 20 - 35 $cmol_c/kg$ for biochar/charcoal both fresh and weathered (Gundale & DeLuca, 2007). The high

CEC of lignite may lead to the retention of $NH_4^+$, thus potentially reducing its availability for nitrification. Commercially, lignite is combined with urea ($CON_2H_4$), as an outer layer on urea granules, and sold as "black urea" (Chapter 3). Because of lignite's ability to retain $NH_4^+$ this "black urea" is identified as a slow release N fertilizer. Therefore, lignite may have the ability to significantly reduce $NO_3^-$ leaching from biosolids, where the lignite may retain $NH_4^+$ that is initially present, or produced as a result of mineralization of organic N. Lignite may also confer other benefits to biosolids-amended soils. Simmler et al. (2013) demonstrated that lignite significantly reduced plant Cd uptake from biosolids-amended soils. Lignite may also offset the potentially toxic effects of high Cu and Zn concentrations that are typically found in biosolids (Lafferty & Hobday, 1990).

Figure 1-7. *Left*: West Coast coal mine, New Zealand; *Right*: Lignite recovered in Southland, mainly disposed of via burning (CANA, 2012).

Qi et al. (2011) showed that heavy metal leaching was well below the biosolids guideline (2003) levels for dewatered sludge application to soil when mixed with lignite. Lapcikova and Lapcik (2006) modified the lignite surface area to increase the $NH_4^+$ sorption from wastewater. Khan et al. (2011) modified the surface of granular lignite increasing $NO_3^-$ sorption. Chassapis et al. (2009) discuss the use of lignite as a soil conditioner, where it can be a source of humic acid, and other organic compounds, or mineral fertilizer (Kucerik et al.,

2003; Pehlivan & Arslan, 2007; Song & Schobert, 1996). However, the addition of lignite to soil is not always beneficial as more minerals (ions) and chemical compounds, such as poly aromatic hydrocarbons (PAHs), may be leached into ground water (Fabianska & Kurkiewicz, 2013; Peuravuori et al., 2006).

## 1.5 Summary of Key Knowledge Gaps:

There is no consensus on how biochar feedstock material influences the reduction of $NO_3^-$ or $NH_4^+$ leaching/sorption.

While biochar is recognized as influencing N cycling in soils, there are conflicting reports on the key properties of biochar that affect $NO_3^-$ leaching. Further work is required to identify biochar characteristics that affect N retention.

Research showed that biochar reduces N leaching from biosolids (Knowles et al., 2011), yet the mechanisms remain unclear. Hypotheses as to why biochar may reduce N leaching are described in sections 1.1.5 and 1.3.1. As yet, there has been no comprehensive study investigating the nature of biosolids-biochar interactions (Mandal et al., 2016). Few studies have investigated the effect of biochar the efficiency of N-fertilizer use.

"Black urea" is a possible slow release N fertilizer. There is one published study by van Vuuren and Claassens (2009), which showed the positive effect of the slow releasing fertilizer, in a trial reported by Agricultural Research Trust (Harare) (2009). Therefore, further studies are warranted on "black urea" or soil amended with both lignite and N-rich materials.

## 1.6 Aim of this thesis

The aim of this thesis is to identify potential low cost carbonaceous soil amendments that could be mixed with biosolids to reduce N mobility. Potentially, this could enable biosolids addition to degraded soils without the risk of excessive $NO_3^-$ leaching.

## 1.7 Objectives of this research

Objective 1: Identifying potentially suitable, low cost carbon-rich materials to mitigate inorganic N leaching from biosolids amended soil (Chapters 1, 2 and 3).

Objective 2: Pyrolyzation and characterization of the different biochars and other potential materials that could be incorporated with biosolids e.g: wood-waste and different lignites. (Chapter 4).

Objective 3: Batch sorption and laboratory leaching experiments; where biosolids are combined with different biochars and wood-waste materials (Chapter 5).

Objective 4: Examine, using a series of batch sorption studies and lysimeter experiments, the effect of lignite on N-fluxes in biosolids-amended soil (Chapter 6).

Objective 5: Quantify the biomass yield and N uptake by rye grass in different greenhouse trials where wood-waste, biochars and lignite are combined with biosolids-amended soils (Chapter 7).

# Chapter 2: Background

## 2.1 Sewage sludge/biosolids

Sewage sludge and biosolids are products of Wastewater Treatment Plants (WTPs). During treatment, sewage is separated into a liquid fraction, which is typically released into waterways or used for irrigation purposes (da Fonseca et al., 2007), while the remaining solids are referred to as sewage sludge or biosolids. Sewage sludge derives from various waste streams that include industrial processes and urban waste, but they exclude agricultural manures and slaughterhouse wastes. There is potential for biosolids to play a role as both a fertilizer and a soil conditioner, since they contain significant amounts of plant nutrients and organic matter. Biosolids may be mixed with other treated and/or stabilized materials (green waste, soil, or pumice) and applied to land.

## 2.2 Magnitude of the biosolids resource

The human population is predicted to reach $9.5\times10^9$ by 2050 (UNNC, 2013), which will result in a proportional increase in the amount of sewage produced. Management of biosolids is therefore a growing environmental issue. Around 41% of the world's population (2.6 billion people) live without basic sanitation, with their untreated sewage disposed of directly into waterways or onto land (Ronald et al., 2008). However, as these countries develop, reticulated water systems and WTPs will be built, thus increasing and concentrating biosolids production. Most developed countries have WTPs linked to elaborate sewage systems and produce large quantities of biosolids each year (Table 2.1). Each country regulates how sewage sludge is disposed of, with the main concerns being the effect of treated human waste to human health, soil fertility, and risk of environmental contamination.

Table 2.1. Countries sewage production and their population in 2008 (Ronald et al., 2008).

| **Country** | **Estimated sewage sludge production (dry metric tons)** | **Population (from *http://www.infoplease.com/ipa/A0004379.html*)** |
|---|---|---|
| Australia* | 330,000 | 36,250,000 |
| Brazil | 372 | 188,078,000 |
| China | 2,966,000 | 1,313,974,000 |
| Turkey | 580 | 70,414,000 |
| Slovakia | 55 | 5,439,000 |
| Hungary | 120 | 9,981,000 |
| Japan | 2,000,000 | 127,464,000 |
| Canada | 550 000 | 33,100,000 |
| Italy | 1,000,000 | 58,134,000 |
| Norway | 87 | 4,611,000 |
| Czech Republic | 200 | 10,235,000 |
| USA | 6,514,000 | 298,444,000 |
| Portugal | 236,7 | 10,606,000 |
| Germany | 2,000,000 | 82,422,000 |
| United Kingdom | 1,500,000 | 60,609,000 |
| Slovenia | 57 | 2,010,000 |
| Finland | 150 | 5,231,000 |
| Netherland | 1,500,000 | 16,491,000 |
| New Zealand* | 74,000 | 4,500,000 |

* Data according to 2014 (ANZBP, 2014).

## 2.3 Production of biosolids

Wastewater influent from domestic and industrial sources undergoes preliminary, primary, secondary, and in some cases, tertiary treatment before sewage sludge is produced and the final effluent is discharged. Figure 2-1 shows a typical WTP where a range of treatment processes are used to produce recycled water and biosolids.

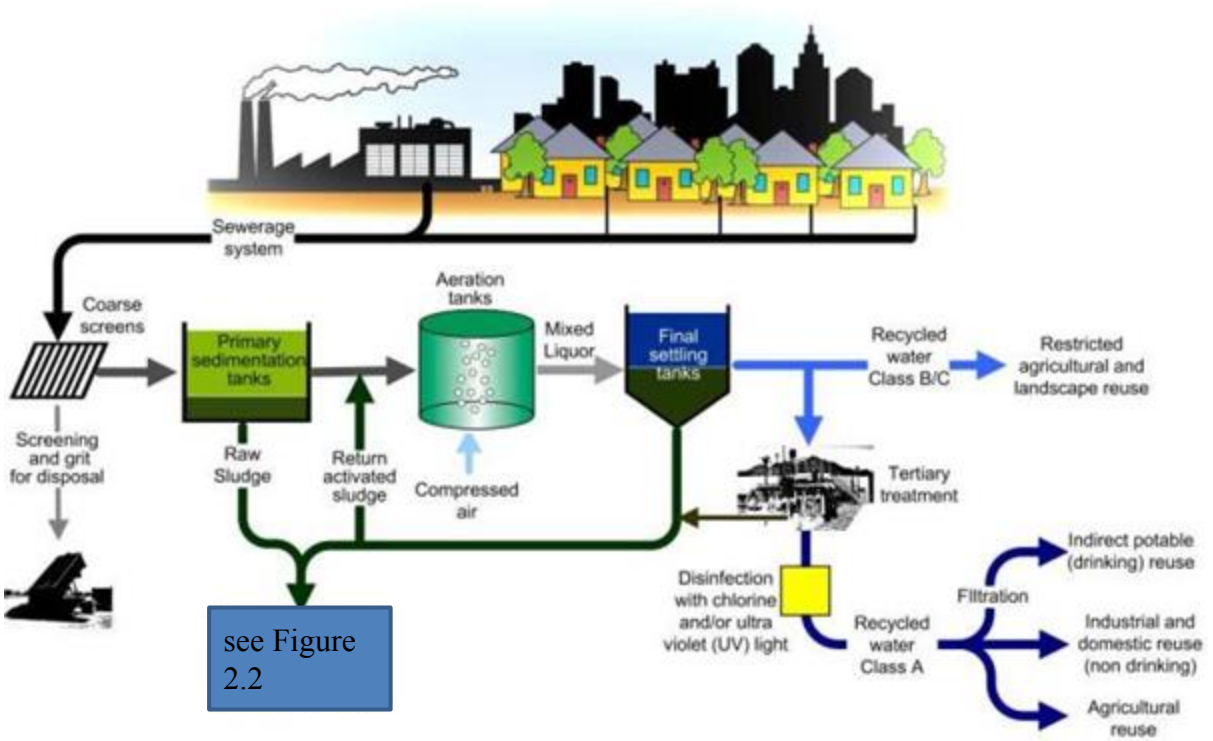


Figure 2-1. A typical WTP produces wastewater sludge and various grades of recycled water (ANZBP, 2014).

During sewage treatment (Figure 2-1), the material is screened to remove large (> 1.5 cm) particles (e.g. glass, stones, plastics or wood). The remaining solid material is then separated sequentially in up to three settling tanks. Water is separated from the solids either by gravity or dissolved air flotation (Jones-Lepp & Stevens, 2007). The separated water may then be treated further and discharged or reused while the sludge can be treated as shown in Figure 2-2. Organic compounds in the sludge are first digested completely by microorganisms, the resultant sludge is then dewatered.

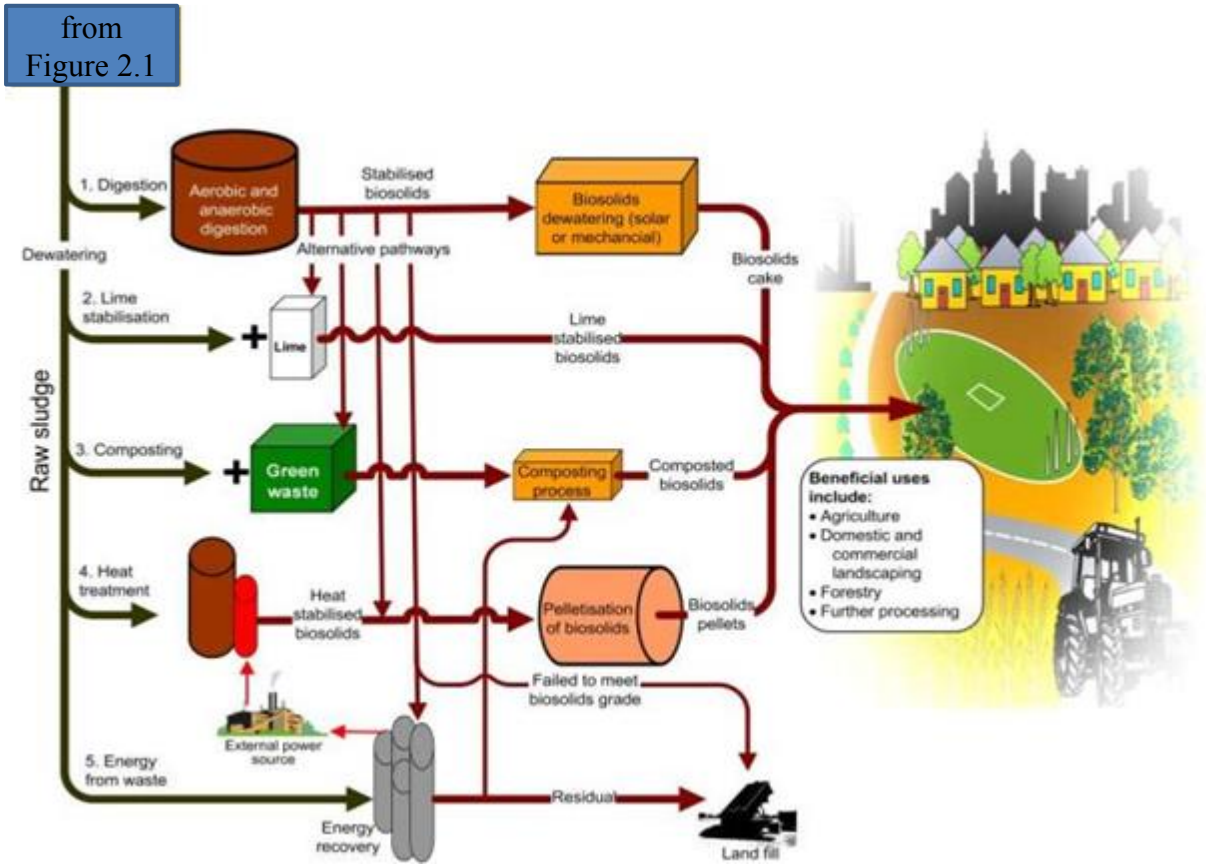


Figure 2-2. Further processing of wastewater sludge, may use digestion, lime stabilization, composting, heat treatment and combustion, producing biosolids of varying quality and end use (ANZBP, 2014).

Digestion may occur under anaerobic or aerobic digesters. This process reduces volatile solids by up to 65% (e.g. fatty acids) and significantly reduces pathogen loading (Jones-Lepp & Stevens, 2007). Conditioning/stabilization –inorganic (lime or ferric chloride) or organic (polymers) are added to reduce pathogen loads (Bina et al., 2004) and increase the pH of the sludge. In addition to chemical stabilization, pathogen counts can be further reduced by heat treatment or UV radiation. Some WTPs use composting and thermal treatment in drying facilities (Jones-Lepp & Stevens, 2007). Composting uses municipal green waste or other bulking agents (e.g. sawdust, sand or pumice) to achieve a compost of about 50% biosolids.

The return of treated waste (liquid or solid) to land, completes the flow of nutrients through the environment (Figure 2-3). This is called “closing the loop”. (Robinson et al., 2011)

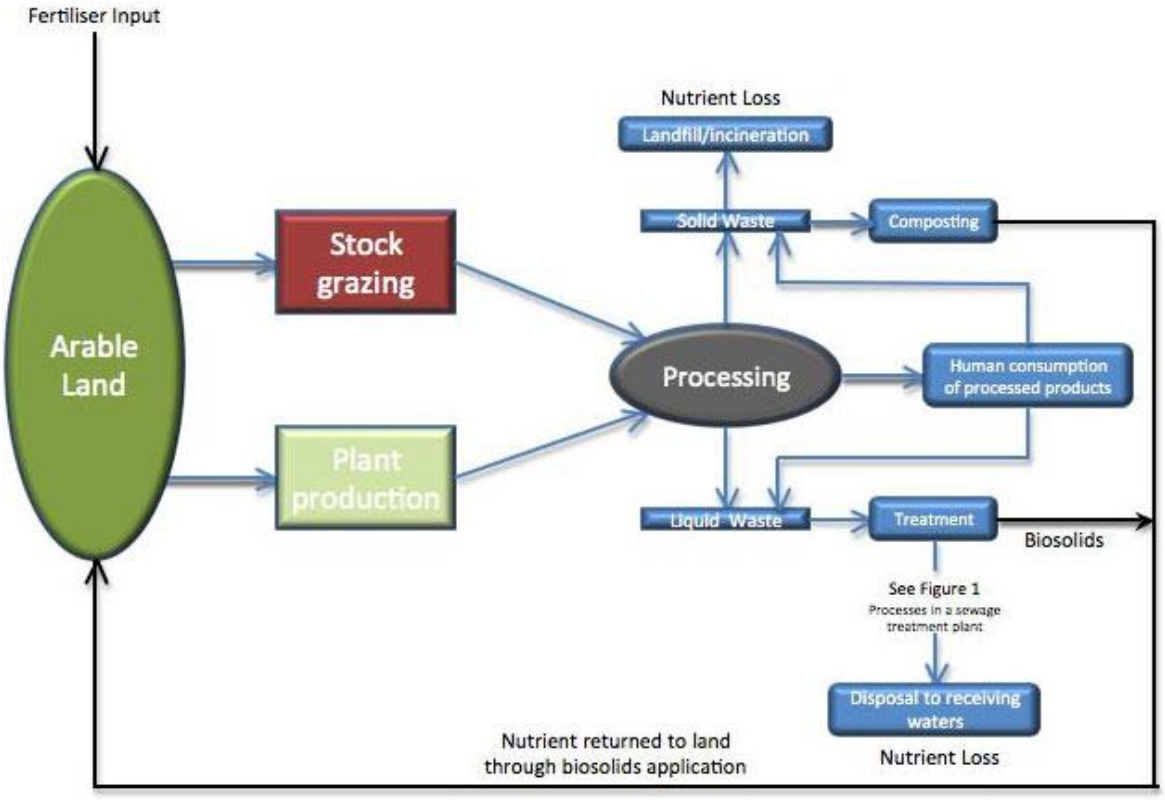


Figure 2-3. Nutrient flows through urban environment (ANZBP, 2014).

## 2.4 Biosolids quality

Often, the quality of biosolids is monitored by central or local Government to reduce the possibility of dangerous compounds entering the "loop". Factory waste may contain heavy metals (such as Ni from stainless steel manufacture or Pb from battery recycling), farm waste may contain residuals from chemical sprays to control weeds, insects or disease control and household sewage may contain significant levels of Zn (Comber & Gunn, 1996) and human pathogens. Only the highest grade biosolids can be used to grow food for human consumption, while lower quality biosolids may be used in plantation forest rehabilitation, mine rehabilitation or used to seal the roads (ANZBP, 2014).

In New Zealand, biosolids are graded according to their quality (NZWWA, 2003). They are labelled "A" and "B" depending on their degree of microbial contamination, Class A biosolids have undergone treatment to reduce pathogens, including pathogenic bacteria, enteric

viruses, and viable helminths ova, to below detectable levels. On the other hand, Class B is defined as biosolids that contain pathogens but at a reduced density (Jones-Lepp & Stevens, 2007). Similarly, another key denote is "a" and "b" mainly refers to the level of contaminants, where "a" contains less contaminant than "b". This classification is used as standard in many countries around the world. In Australia, biosolids are classified as $T_1$, $T_2$ and $T_3$ (microbial level) and $C_1$ and $C_2$ (Chemical) where $T_3$ and $C_2$ is not suitable for any sort of use/application, because it contains high levels of microbes and chemical contaminants (EPA-VA, 2004).

## 2.5 Composition of biosolids

The organic matter content of biosolids is typically 75% by dry weight and includes nutrients that include nitrogen (N 3.5% w/w), phosphorus (P 3.5% w/w), and potassium (K 0.2% w/w). Biosolids also contain trace elements including Zn ~1000 mg/kg, Cu ~500 mg/kg, Ni ~40 mg/kg, Pb ~200 mg/kg, and Cd ~3 mg/kg and also some pathogens (e.g. *E.coli*, *Salmonella*, more examples are in Table 2.5) and some residues of organic contaminants (e.g. polychlorinated biphenyls, DDT, more examples are in Table 2.7), pharmaceuticals and personal care products (PCPs) e.g. Triclosan, Ibuprofen (Ronald et al., 2008) and more examples are shown in Table 2.4. The effect of these contaminants were discussed in Section 2.5.2. Biosolids composition varies with decomposition stage (Table 2.2) and source (Table 2.3).

Table 2.2. Chemical analysis of the biosolids at different stages of aging (adopted from: Bernal et al. (1998).

| | Initial mixture | [a]Sampled at the end of decomposition | [b]Matured compost |
|---|---|---|---|
| pH ($H_2O$) | 7.6 | 8.0 | 7.3 |
| Electrical conductivity (S/m) | 0.39 | 0.50 | 0.67 |
| CEC (mmol /kg) | 535 | 1007 | 1244 |
| Organic Matter (%) | 82 | 65 | 65 |
| Organic C (g/kg) | 439 | 360 | 356 |
| Total N (g/ kg) | 21 | 37 | 38 |
| Organic N (g/kg) | 20 | 36 | 34 |
| C/N ratio | 21 | 10 | 9 |
| $NH_4^+$-N (mg/ kg) | 802 | 208 | 182 |
| $NO_3^-$-N (mg/ kg) | <1 | 526 | 4192 |

[a] under 55°C with aeration sampled after 49 days; [b] after it was stabilized by decomposition, 2 months later this was sampled.

Table 2.3. Chemical properties of sewage digests from different sources (adopted from: (Rigby & Smith, 2013).

| Properties[a] | Biosolids[b] | Municipal solid waste[c] | Animal slurry[d] | Food waste[e] |
|---|---|---|---|---|
| DS (%) | 29 | 29 | 5 | 17 |
| OM (%) | 60 | 42 | 38 | 86 |
| pH | 7.2 | 8.8 | 8.2 | 4.4 |
| Total P (g/ kg) | 28 | 4 | 6 | 4 |
| Total K (g/ kg) | 1.9 | 5.1 | 37.6 | 5.4 |
| Total Mg (g/ kg) | 3.0 | 8.0 | 6.3 | 2.4 |
| Total S (g/ kg) | 12 | 8 | 6 | 3 |
| Total N (%) | 4.6 | 2.3 | 11.3 | 3.5 |
| $NH_4$–N (mg/ kg) | 3400 | 3360 | 52,500 | 2800 |
| $NO_3$–N (mg/ kg) | 82.1 | 191 | 0.43 | 0.19 |
| Organic N (%) | 4.22 | 1.96 | 6.00 | 3.22 |
| Mineral N (%) | 9.09 | 15.3 | 46.6 | 8.01 |
| C to N ratio | 7.5:1 | 11:1 | 4:1 | 14:1 |

[a] Values on a dry solids (DS) basis.
[b] Dewatered, mesophilic anaerobically digested biosolids.
[c] Dewatered, mesophilic anaerobically digested organic fraction of municipal solid waste.
[d] Liquid, anaerobic co-digestate of food and animal slurry.
[e] Liquid, thermophilic aerobically digested food waste.

### 2.5.1 Heavy metals

"Heavy metals" is a generic term for elements with a density >5 (Arsenic (As) is the exception). Most are associated with contamination and all are potentially toxic to animals and/or plants. Common elements considered include As, Cd, chromium (Cr), Cu, mercury (Hg), Ni, Pb and Zn. Industrial wastewater is often the major source of heavy metals in sewage.

Wastewater from surface treatment processes (e.g., electroplating and galvanizing industries) can be a source of metals such as Cu, Cr, Ni and Zn. Urban activities including stormwater drainage, business effluents (e.g., car washes, dental clinics), atmospheric deposition, and traffic related emissions (e.g. vehicle exhausts, brake linings, tyres, asphalt wear, petrol/oil leakage), which are transported with stormwater into the sewage system, are also a source of heavy metals. Most Cu originates from Cu piping; Zn generally comes from household products (since it is a component of skin creams, ointments, makeup, deodorant, talcum powder, shampoo, and aftershave) (Adriano, 2001; Haynes et al., 2009). Table 2.4 shows typical concentrations of heavy metals commonly encountered in biosolids.

Table 2.4. Heavy metals and typical concentrations found in biosolids (Haynes et al., 2009).

| Element | Concentrations (mg/kg) dry weight |
|---|---|
| Arsenic (As) | 1–20 |
| Cadmium (Cd) | 1–70 |
| Chromium (Cr) | 50–500 |
| Cobalt (Co) | 5–20 |
| Copper (Cu) | 100–800 |
| Lead (Pb) | 100–600 |
| Mercury (Hg) | 1–10 |
| Nickel (Ni) | 10–200 |
| Selenium (Se) | 5–10 |
| Zinc (Zn) | 1000–3000 |

### 2.5.2 Pesticides, pharmaceuticals and other organic contaminants

Industrial by-products contribute contaminants such as polychlorinated biphenyls (PCBs), dioxins, poly-aromatic hydrocarbons (PAHs), pesticides, herbicides, chemicals found in day to day house hold cleaning products, cosmetics, mouthwash (e.g. polybrominated diphenyl ethers (PBDEs), nonylphenol, linear alkyl sulfonate, pharmaceuticals) (Ronald et al., 2008). Pesticide residues accumulate in the body fat of grazing animals, and enter humans via the food chain and are then excreted.

### 2.5.3 Endocrine Disrupting Compounds (EDCs)

Endocrine Disrupting Compounds (EDCs) are a broad class of chemicals that include natural estrogens, androgens such as testosterone, artificial synthetic estrogens or androgens (Blair et al., 2000), compounds used in industry such as bisphenol A, and nonylphenol (Ramamoorthy et al., 1997). They interfere with the hormone system in mammals and can cause tumours, birth defects, and developmental disorders (Liu et al., 2009). Such chemicals have been found in wastewater, surface waters, sediments, groundwater, and even drinking water. Therefore, WTPs are a major source of EDCs, particularly those that produce estrogen-like responses (Liu et al., 2009). While EDCs have been attributed as a cause of reproductive disturbance in humans and wildlife (Campbell et al., 2006), many are degraded during the treatment process (Liu et al., 2009).

EDCs from Personal Care Products (PCPs) were widely identified in surface waters around the United Kingdom, parts of Europe and North America, and in high concentrations downstream of WTPs (Ronald et al., 2008).

### 2.5.4 Microbial presence

Sewage sludge and biosolids can contain a wide variety of pathogens, including bacteria, viruses, parasites (helminths/protozoa), and fungi. Pathogens of most concern are passed by the faecal-oral route and include *Salmonella spp*, enteric viruses, helminth ova and oocysts of protozoa (Bina et al., 2004). *Escherichia coli* (*E. coli*) is the indicator species for the presence of bacterial pathogens in biosolids, where high counts of Colony Forming Units (CFU) indicate that other human pathogens are likely present (Gary et al., 2011). *Salmonella spp.* are common in the environment, but are easily controlled through good food hygiene practises. However, Smith (1995) showed that the presence of *Salmonella spp.* does not increase when biosolids are used properly (e.g. application depth, season, wind flow, timely harvest) in agriculture. Protozoa found in sewage include *Entamoeba histolytica* (amoebic

dysentery), *Giardia entestinalis* (gastro-enteritis), *Cryptosporidium* (gastro-enteritis) and *Balantidum coli* (gastro-enteritis). These organisms generally occur as cysts, which are inactivated by heat and/or lime treatment during biosolids production (NZWWA, 2003). Some common pathogens present in Class B biosolids are listed in Table 2.5. Treatment processes, such as anaerobic digestion, can considerably reduce, but not eliminate the pathogen load. Faecal coliform counts in stabilized sludge can still be high, up to $10^5$/g dry sludge and potential contamination of food crops, surface and ground waters by run-off of pathogens from land-applied sewage is a potential public health risk.

Table 2.5. Approximate concentrations of pathogens in Class B biosolids and animal manures. Values are in colony- or plaque-forming units (CFU and PFU, respectively) (Gary et al., 2011).

| Organism | Source | CFU or PFU $g^{-1}$ | References |
|---|---|---|---|
| **Bacteria** | | | |
| *Campylobacter jejuni* | Manure | 1400 | Chinivasagam et al. (2004), Hutchinson et |
| | Biosolids | 2 | Jones et al. (1990) |
| *E. coli* O157:H7 | Manure | 110 | Berry and Miller (2005), Hutchinson et al. |
| | Biosolids | <1 | Pepper et al. (2010) |
| *Listeria monocytogenes* | Manure | 210 | Hutchinson et al. (2005), McLaughlin et al. (2009) |
| | Biosolids | 20 | Garrec et al. (2003) |
| *Salmonella* | Manure | 180 | Chinivasagam et al. (2004), Hutchinson et al. (2005), McLaughlin et al. (2009) |
| | Biosolids | 50 | Zaleski et al. (2005), Gerba et al. (2008), Pepper et al. (2010) |
| **Viruses** | | | |
| *Adenoviruses* | Biosolids | 20 | Pepper et al. (2010) |
| *Enteroviruses* | Biosolids | <1 - 30 | Guzman et al. (2007), Lang et al. (2007), Pepper et al. (2010) |
| **Parasites** | | | |
| *Cryptosporidium* | Manure | 3 | Hutchinson et al. (2005) |
| | Biosolids | 2 | Guzman et al. (2007) |

## 2.6 Fate of biosolids

### 2.6.1 Discharge into waterways

Discharge of sewage sludge to the sea is banned in most developed countries, but it is common practice in many poor countries with minimal sanitary infrastructure. In some parts of Asia, Central and South America, and Africa untreated sewage sludge is dumped directly into natural water bodies (rivers, lakes and oceans), resulting in the transmission of human diseases, and pollution of the environment (Ronald et al 2008). Some developed countries treat their sewage sludge before discharge into waterways. According to ANZBP (2014), 10% of biosolids produced in New Zealand are discharged into oceans.

### 2.6.2 Incineration

Incineration of biosolids is standard practice in large, densely populated areas of some technologically advanced countries (Ronald et al. 2008). This process greatly reduces the volume of excreta and wastewater sludge by rapidly oxidizing the organic matter. However, it requires a large capital investment in infrastructure and ongoing fuel costs. It also contributes to air pollution and the emission of greenhouse gases (levels will be much less than combustion of fossil fuel). Japan incinerates more than 70% of its wastewater sludge and the ash is used in construction materials (Fujiki) (Ronald et al., 2008). In the Netherlands and Germany, the rates are 58% (Kreunen) and 34% (Schulte), respectively (Ronald et al., 2008). Slovenia dries much of its wastewater sludge and then sends 50% out of the country (to Germany, for example) for disposal in incinerators (Grilc) (Ronald et al., 2008). In Canada, about one third of the sludge is incinerated, and in the USA, 15% (Ronald et al., 2008). Incineration may be a low cost option for biosolids disposal, because the average cost for biosolids landfill application ranges between NZ$ 250 -300 per ton (WCC, 2008).

### 2.6.3 Other uses for sewage sludge/biosolids

Elsewhere, biosolids are used to make bricks, construction materials, biofuels, in glass manufacture, as a fuel substitute in cement works, as an additive to road bases and jewellery (ANZBP, 2014).

### 2.6.4 Landfilling

Dumping of untreated excreta, septage (septic tank waste) and wastewater sludges on land is common in undeveloped countries but dumping poses an environmental problem, and a risk to human health. On the other hand, modern landfills are no longer a cheap and easy method of disposal. In developed countries, landfill space has become more expensive, with stricter regulations regarding what may be landfilled, and operations are more costly. Dewatering of wastewater sludge is the only requirement before placing it in a landfill (with no regulation of microbial/chemical contaminant levels). Therefore, this represents the cheapest option in a developing country where landfills are allowed. Some European Union countries (e.g. Germany and France) legally banned landfilling with biosolids (Ronald et al., 2008). Other countries (e.g. the province of Québec in Canada) discourage landfill application with additional taxes (Ronald et al., 2008). In Austria, the minimum requirements for landfilling state that the wastewater sludge must contain at least 5% organic matter (Ronald et al., 2008). In New Zealand, 78% of the biosolids produced in 2011 were disposed of in landfills, this reduced to 60% in 2012 ANZBP (2014).

### 2.6.5 Land application of biosolids

Many countries oppose the application of biosolids to agricultural land. However, biosolids have significant fertilising and soil conditioning properties (increasing nutrient and water holding capacity). In Australia, land application of the highest-grade biosolids (combination of $T_1$ and $C_1$) is permitted with unrestricted use, including in residential areas and

can be applied to human food crops that are consumed raw. On the other hand, lesser grade biosolids ($C_2$,$T_2$ and $T_3$) have restricted uses and require controls on public access to application sites, withholding periods for stock or human food crops, forestry, and land rehabilitation (EPA-VA, 2004).

The grade of biosolids, determines the withholding period following land application (EPA-VA, 2004). In Australia only $T_1$ grade biosolids are allowed to be in direct contact with human food crops, e.g. carrots, lettuces, strawberries, mushrooms. Grade $T_2$ biosolids application is permitted on crops, which are harvested above 1 m above the soil surface, and the biosolids application should not take place within a period of three summer months before the harvest. This regulation applies to grazing land as well. There are 2 yr, 60 d or 30 d withholding periods for $T_3$ cattle and poultry farming or $T_2$ for cattle farming (respectively) applied to grazing lands in Australia.

Evidence indicates that biosolids can be beneficially recycled to land, provided the treatment and application of biosolids is subject to adequate management control (NZWWA, 2003). Biosolids application rates, in terms of N inputs, should not exceed the agronomic N needs of the crop. Surface application of biosolids to animal grazing grassland has been identified as a potential pathway for human exposure to contaminants in the biosolids (Section 2.5.2). In New Zealand limits for heavy metals and organic contaminants that may be applied to land have been previously determined (NZWWA, 2003); Table 2.7). Some beneficial use options for biosolids other than landfills are shown in Table 2.6.

Table 2.6. Potential beneficial use options for municipal biosolids and municipal sludge (CCME, 2012).

| Potential Beneficial Use Option | Examples |
|---|---|
| Compost and Soil Products (e.g., topsoil and compost) | • Municipal biosolids, used as an ingredient in topsoil and compost, provide a source of nutrients and organic matter, which supports plant establishment and growth.<br>• Municipal biosolids can be used in the development of a final cover for placement on landfills to mitigate fugitive methane ($CH_4$) emissions |
| Agricultural Land and Forestry Applications | • Municipal biosolids provide macronutrients (e.g. N and P) and micronutrients (e.g. Cu, Co, Cr, and Zn).<br>• Land application of municipal biosolids can supplement and potentially reduce other fertilizer use.<br>• Municipal biosolids contain organic matter that improves soil physical properties including porosity, bulk density, and water holding capacity. |
| Land Reclamation | • Municipal biosolids serve as a source of nutrients and organic matter to help promote soil development and the establishment of vegetation on degraded sites.<br>• Municipal biosolids can be used at mine sites to assist in reclamation initiatives. |
| Energy production | • Biogas generated during anaerobic digestion of municipal sludge can be captured and used for heating or to generate electricity.<br>• Energy capture in the form of heat from combustion of municipal sludge can be used to generate electricity and steam. |

Table 2.7. Soil allowed limits after application of biosolids and biosolids classification by contaminant levels (NZWWA, 2003).

| **Parameter** | **Soil limit or ceiling concentrations (mg/kg dry weight)** | **Biosolids limits** | | |
|---|---|---|---|---|
| | | **Grade a max. concentration (mg/kg dry weight)** | | **Grade b max. concentration (mg/kg dry weight)** |
| **Metals** | | Until 31/12/12 | After 31/12/12 | |
| As | 20 | 20 | 20 | 30 |
| Cd | 1 | 3 | 1 | 10 |
| Cr | 600 | 600 | 600 | 1500 |
| Cu | 100 | 300 | 100 | 1250 |
| Pb | 300 | 300 | 300 | 300 |
| Hg | 1 | 2 | 1 | 7.5 |
| Ni | 60 | 60 | 60 | 135 |
| Zn | 300 | 600 | 300 | 1500 |
| **Organics** | | | | |
| DDT/DDD/DDE | 0.5 | 0.5 | 0.5 | 0.5 |
| Aldrin | 0.02 | 0.02 | 0.02 | 0.2 |
| Dieldrin | 0.02 | 0.05 | 0.02 | 0.2 |
| Chlordane | 0.02 | 0.02 | 0.02 | 0.2 |
| Heptachlor and Heptachlor epoxide | 0.02 | 0.02 | 0.02 | 0.2 |
| Hexachlorobenzene (HCB) | 0.02 | 0.02 | 0.02 | 0.2 |
| Hexachlorocyclohexane (Lindane) | 0.02 | 0.02 | 0.02 | 0.2 |
| Benzene hexachloride (BHC) | 0.02 | 0.02 | 0.02 | 0.2 |
| Total polychlorinated biphenyls (PCBs) | 0.1 | 0.2 | 0.2 | 0.2 |
| Total dioxin TEQ[4] | 0.00001 | 0.00003 | 0.00003 | 0.00005 |

## 2.7 Benefits of applying biosolids to land

Inorganic N (i.e. $NH_3$, $NO_3^-$ and $NH_4^+$) contained in biosolids is potentially available for plant uptake when municipal biosolids are applied to land. The inorganic N that is actually available to plants is the total inorganic N in the biosolids minus any lost to other aspects of the N cycle through volatilization, immobilization or leaching (Prasad & Power, 1997). Organic N contained in the municipal biosolids is not directly available to plants. However,

following application to land a fraction of the organic N will mineralize (i.e., be transformed to available inorganic forms by microorganisms in the soil) in the year of application (Prasad & Power, 1997). The amount of potentially plant available N in the first year is the sum of the inorganic N plus the mineralized organic N.

A site specific nutrient management plan requires the consideration of: (i) the mineralization rate of the municipal biosolids, (ii) the volatilization rate of ammonia-N, (iii) nitrate-N concentrations in the municipal biosolids at application time, (iv) crop type, and (v) soil fertility level (Haynes et al., 2009).

Korboulewsky et al. (2002) showed that biosolids application rates of 10, 30 and 90 t/ha on a fresh weight basis, significantly increased the soil organic matter content (up to 3000 mg/kg) in a vineyard soil 18 months after the biosolids application. The soil inorganic N concentrations increased by 5-26 kg N/ha. Higher rates (90 t/ha) posed a risk of N leaching to surface and ground waters and it was recommended that 10 t/ha was the appropriate rate for the associated land management in order to minimise $NO_3^-$-N leaching (Korboulewsky et al., 2002).

In Greece, Samaras et al. (2008) studied soil fertility, cotton yield and N leaching after multiple applications of biosolids. The biosolids were incorporated to a soil depth of 15 cm at 10, 30 and 50 t/ha during four consecutive years. Soil organic matter, soil nutrients and soil physical properties improved, but an increase in soil electrical conductivity was noted, which could affect plant growth (especially salt sensitive plants). However, the cotton plant is salt tolerant. Higher biosolids application rates produce high soil $NO_3^-$ -N concentrations, which are beyond the requirements of the crops and result in leaching. Therefore, Samaras et al. (2008) suggested a safe rate of application was 10 t/ha. Their comparison of the effect of biosolids with inorganic fertilizer showed that inorganic fertilizer could be replaced by the biosolids.

Nash et al. (2011) reported on a three year trial of pasture and vine growth following the application of biosolids in southeastern Australia. They showed that soil Cd, Cu and Zn concentrations increased linearly with biosolids application rates (0.5 - 4.5 kg N/ha); however, these concentrations remained under the soil quality guidelines. For pasture soils, there was a marginal increase in total C and N, and a significant increase in total P, while in the vineyard soil there was a significant increase in total C, N and P. Soil microbial populations were not affected by biosolids application on either the pasture or vineyard soils.

Lavado (2006) applied biosolids at 7 t/ha and 14 t/ha to a sunflower farm in Argentina. There was an increase in plant available P and soil $NO_3^-$-N, and sunflower yield, but the sunflower seed oil content, nutrients and trace-metal concentrations of the oil, and individual grain weight were not affected.

Other studies have also showed the benefit of biosolids application to agricultural land/food crops/farm (Binder et al., 2002; Brenton et al., 2007; Rajendram et al., 2011). These studies indicate that an application rate ranging between 10-30 t/ha avoid P and N leaching from soils, mitigating the negative impacts to the environment, soil and human health.

New Zealand is dependent on its dairy industry and other land-based sectors. New Zealand exports are sold as being produced in a clean, green land and the application of biosolids may compromise this quality or the publically perceived quality. While the use of biosolids for food production may be distasteful to the general public, the selective use of biosolids to rebuild some degraded soils may be better accepted (Wang et al., 2003). Thus, research detailing benefits of biosolids and its safety is necessary for public acceptance of land application of biosolids.

## 2.8 Fate of biosolids-borne contaminants after the land application

### 2.8.1 Heavy metal accumulation

There are public and environmental health issues involved with the use or disposal of biosolids as they contain heavy metals and chemical contaminants. Repeated application of biosolids increases the risk of heavy metal accumulation in soil. The main metals of concern from a human health perspective are Cd, Pb and Hg (Smith, 1995). Crops cannot take up Pb and Hg, while Cd can be accumulated. According to Chaney and Oliver (1996) biosolids with high concentrations of Zn can reduce crop Cd uptake due to an antagonistic effect between these two metals. Table 2.7 details the heavy metals and other compounds found in two different biosolids grades and their limitations.

### 2.8.2 Other toxins (EDCs, pharmaceuticals and pesticides)

According to Smith (1995), there is minimal risk to human health from the organic contaminants listed in Table 2.7 when crops are grown in biosolids-treated soils, because there is little or no plant uptake (except for some PCBs). The U.S Environmental Protection Authority (EPA) gathered soil samples from 84 land-based biosolids application areas and analysed for the presence of pharmaceuticals/organic chemicals. Their results (Figure 2-4) showed that Triclosan was found in 79 sampling sites, and three compounds, ciprofloxacin, diphenhydramine, and triclocarban were found in 84 sites (Shinbrot, 2012). As mentioned before these compounds are identified similarly as EDCs.

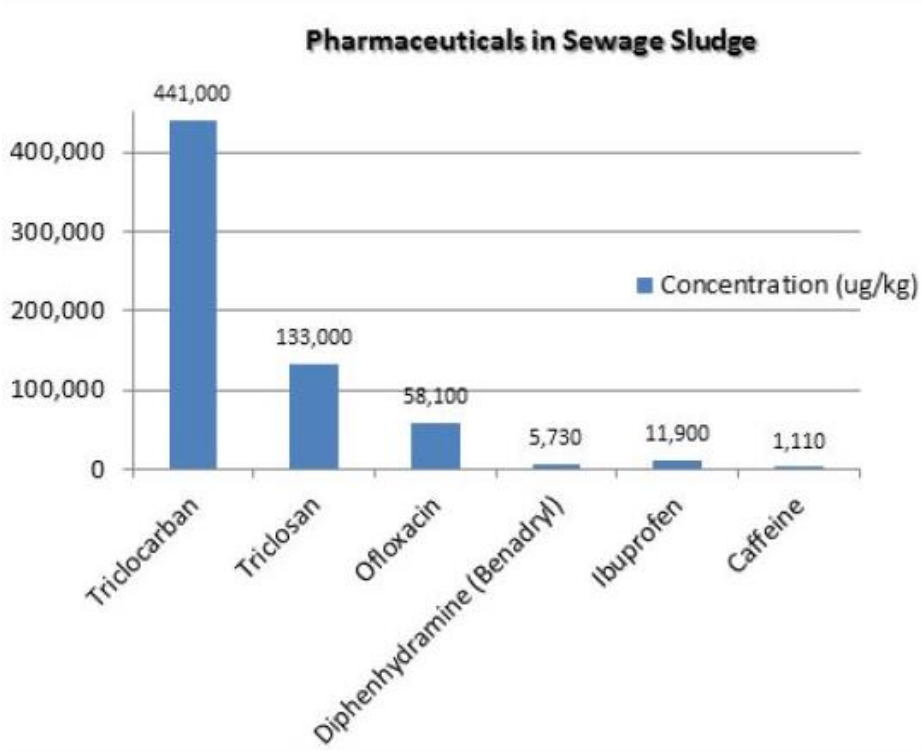


Figure 2-4. Pharmaceutical residues in the biosolids (Shinbrot, 2012).

### 2.8.3 Pathogens

The application of biosolids to land also raises concerns about pathogenic microbial contamination. Human health is threatened from untreated excreta, wastewater, and wastewater sludge containing pathogens and microorganisms that can cause disease. In developed countries, the risk is much reduced, because of the presence of WTPs, food hygiene regulations, and established and funded medical infrastructure. Poor countries, which lack such infrastructure and regulations, are at much higher risk from the same pathogens.

The long term effect of biosolids application can cause the accumulation of organic contaminants (mentioned above), some of which have anti-microbial properties, which can harm/interfere with the function of beneficial soil microbes (Ronald et al., 2008).

Zerzghi et al. (2010) studied a long-term trial, where biosolids had been applied for 20 consecutive years (Class B biosolids, 8 and 24 t/ha) to soil in Tucson, Arizona. They grew cotton (*Gossypium hirsutum* L.) followed by the first application. Bacterial diversity was

investigated by analysing the soil surface (0-30 cm). Extracting and analysing the total bacterial community showed that the number of Genera (identifiable > 96%) increased at the 24 t/ha application when compared to the control (no amendment). However, the identified bacterial communities were typical of the bacterial diversity found in control soils. They concluded that long-term application of Class B biosolids had no deleterious effect on soil microbial diversity. Similar results was shown by Prasad and Power (1997), in their four year experiment conducted in the Southwest United States.

Land application of biosolids can, however, significantly change the structural, diversity of the microbial community (Sullivan et al., 2006). Monitoring the soil microbial community can be a useful way to manage the sustainability of soil receiving biosolids (Gilmour et al., 2003).

### 2.8.4 Nitrous oxide and air quality issues

The Intergovernmental Panel on Climate Change (IPCC) document on waste management has mentioned landfills as one source of nitrous oxide ($N_2O$) emission. The major greenhouse gas (GHG) emissions from the waste sector are landfill methane ($CH_4$) and, secondarily, wastewater $CH_4$ and $N_2O$. In addition, the incineration of fossil carbon results in minor emissions of $CO_2$ (Bogner et al., 2008). Methane and $N_2O$ are formed when organic materials such as excreta, wastewater, wastewater sludge, and biosolids decompose in anaerobic (or almost anaerobic) conditions (Beecher et al., 2009). Spokas et al. (2006) studied $CH_4$ emission in landfills and showed rates ranged from 0.09 to > 417 mg $CH_4$ $m^2$/ h.

When biosolids are applied to land, they release less $CO_2$ than when they are incinerated. In addition to $CO_2$, incineration also releases $N_2O$ (Bogner et al., 2008). The IPCC default value is 563 g $N_2O$-N/t biosolids in a land application (Beecher et al., 2009). Borjesson and Svensson (1997) measured $N_2O$ emissions from Swedish sewage sludge landfills. Sewage sludge that was surface-applied had higher $N_2O$ emissions ranging from 1.23 to 35.7 mg $N_2O$-

$N/m^2/h$, than sewage sludge filled sites covered with soil where emissions ranged from -0.011 to 16.7 mg $N_2O$-$N/m^2/h$. They collected gas samples 5 times during the experimental period of 16 months, which involved almost 12,100 t of sewage sludge. This study also showed that fresh sewage sludge used as land cover released higher levels of $N_2O$ emissions than aged sludge. However, they commented that the sewage sludge could be a minor source of $N_2O$ compared to the national level of $N_2O$ emission.

These results indicate that biosolids used as landfill cover can potentially release $N_2O$. It is unlikely that landfilled biosolids would release $N_2O$ at the same or a similar rate to materials applied to the soil surface, as the environment within a landfill is more oxygen deficient than the environment at the landfill surface, leading to further reduction of $N_2O$ to $N_2$. Table 2.8 shows the air pollutants released in two different circumstances where biosolids were involved.

Table 2.8 Rates of $N_2O$ emissions from different types of combusted biosolids. (source: (Beecher et al., 2009)

| Country | Biosolids | g $N_2O$/Mg Biosolids | Weight basis |
|---|---|---|---|
| Japan | Dehydrated | 900 | Wet weight |
| | Lime sludge | 294 | Wet weight |
| | Cake | 1520-6400 | Dry weight |
| Germany | Cake | 990 | Dry weight |
| Montreal | Cake | 1-5 kg | Dry weight |
| IPCC default | - | 990 | Dry weight |
| IPCC default | - | 900 | Wet weight |

## 2.9 Nitrate leaching from biosolids

Nitrate ($NO_3^-$) is a negatively charged ion, not retained by the normally negatively charged soil particles. Following application of N–rich soil amendments, $NO_3^-$ can leach from the soil and into surface or ground waters (Binder et al., 2002). High concentrations of $NO_3^-$ in waterways are deleterious to the health of humans and promotes eutrophication (Brenton et al., 2007).

The availability and total N content in biosolids/wastewater varies greatly depending on the origin of the waste and treatment process. Typically, biosolids comprise an average total N content of ~5%. The main forms of N in biosolids are organic N (~ 95%), $NO_3^-$ (~4%), and $NH_4^+$ (~ 1%) (Henry et al., 2000; Lee et al., 2001). The $NO_3^-$ form is highly mobile in soil and can leach through the soil profile to contaminate surface/ground water. The biosolids application rate is determined by the N loading calculation, which is based on a balance between the inorganic-N fraction in the biosolids and the N assimilative capacity of the ecosystem.

Bernal et al. (1998) reported that composted biosolids provided a better resource of N (a stable N supply for the plant) and consequently a better plant growth response than raw or digested sewage material because of unstable mineral N. Henry et al. (2000) studied the N mineralization rate of biosolids, using porous ceramic cups, to determine the effect of biosolids application rate, type of biosolids (dry and wet) and soil incorporation. There were only slight differences in mineralization between wet and dry biosolids, and no difference between the biosolids application rates. Sommers et al. (1980) noted that N mineralization rates of anaerobically digested biosolids are 20% (total N) for the first year. However, other studies showed it would have been nearly 74% (Gilmour et al., 2003). The rate of organic N mineralization from the biosolids is important to know when estimating the safe rate of biosolids application and plant available N. Excessive mineralization leads to high $NO_3^-$ leaching in addition to plant uptake (Henry et al., 1994). Therefore, it is important to understand the fate of N in soils treated with biosolids for both plant nutrition and managing the environmental risk of $NO_3^-$ leaching.

### 2.9.1 Influence of the N cycle to nitrate leaching

Most of the total N in biosolids is organic N (approximately 95%), which is unavailable to plants (Henry et al., 2000). When biosolids are mixed and surface-applied with soil, soil microbes mineralize the organic N to form $NH_4^+$, which is plant-available.

#### 2.9.1.1 Mineralization and immobilization

In biosolids, the rate of N mineralization is related to the total organic N content. A large proportion of the biosolids organic N is thought to be proteinaceous in origin and this fraction represents a labile pool of organic N (Haynes et al., 2009). Nitrogen mineralization from biosolids is mainly a consequence of catabolism of the protein pool rather than decomposition of the material as a whole (Rowell et al., 2001). However, when biosolids are incorporated in soil these two process are mainly influenced by the C/N ratio of organic matter present in the soil, so that a low C/N ratio will lead to a high mineralization rate and vice-versa (Burgos et al., 2006). Immobilization of N is defined as the transformation of inorganic N compounds ($NH_4^+$, $NH_3$, $NO_3^-$ and $NO_2^-$) into the organic state. Soil organisms assimilate inorganic N compounds and transform them into the organic N constituents of their cells and tissues (McLaren & Cameron, 1996).

#### 2.9.1.2 Nitrification

Nitrification is the aerobic conversion of $NH_3$ to $HNO_2$ according to Suzuki et al. (1974) (see Equations 1.1, 1.2 and 1.3 in Chapter 1) and this is further oxidised to $NO_3^-$. Suzuki et al. (1974) showed that $NH_3$ is the substrate generally used by microbes, rather than $NH_4^+$ and growth of these nitrifiers is affected by the ratio of $NH_3$/ $NH_4^+$.

#### 2.9.1.3 Denitrification

Denitrification is the stepwise reduction of $NO_3^-$ to $N_2$, carried out by denitrifiers such as *Pseudomonas spp., Bacillus spp.,* and *Thiobacillus spp.* These microbes are facultative

anaerobes that are able to use $NO_3^-$ in place of oxygen. Reductase enzymes catalyse each step in Equation. 2.1.

$$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O \rightarrow N_2 \qquad \text{[Equation 2.1]}$$

Denitrification may be performed by nitrifiers in a process known as nitrifiers-denitrification or by true nitrifiers (Wrage et al., 2001) (Figure 2.5).

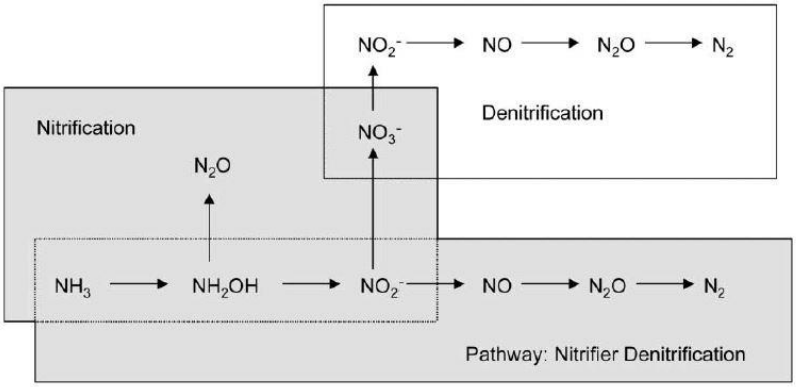


Figure 2-5. Summarized pathways to mineral N transformation in soil (Wrage et al., 2001).

# Chapter 3: Background on potential agents to mitigate N leaching from biosolids

## 3.1 Mitigation of N leaching

Many studies have examined methods to mitigate N leaching. Briefly these include, (i) strategically managed fertilizer regimes that include slow-release fertilizers and or nitrification inhibitors, (ii) soil management, (iii) crop management, and (iv) water management (Zhaohui et al., 2012). Fertilizer management requires that application rate, season, and crop type are all taken into consideration. Normally N fertilizer can be replaced by slow-release fertilizer such as coated urea (Black et al., 1985). On the other hand nitrification inhibitors (Dicyandiamide) commonly known as DCD can be incorporated with N fertilizer to mitigate nitrate losses from the applied fertilizer. My aim is to identify low cost, readily-available material for incorporation in soil to mitigate N leaching.

## 3.2 Biochar or charcoal and wood-waste

### 3.2.1 Wood-waste

Wood-waste is a by-product of the timber industry and deforestation, and is readily available worldwide and year-round. Worldwide, mostly in temperate and sub-tropical areas, deforestation is increasing rapidly to fulfil the need for agricultural land as global food demand increases (Chakravarty et al., 2012).

Commercial logging operations remove trees for timber or pulp. Gerwing et al. (1996) showed a commercial timber logging operation, followed by sawmilling, created approximately 24.7 $m^3$/ha of wood-waste. Wood-waste is left at the logging site and logs go to sawmills where further wood-waste (sawdust) is created. In New Zealand wood-waste is readily available for little or no cost (Schipper & Vojvodic-Vukovic, 2000). In this thesis, wood-waste/sawdust specifically refers to *untreated* sawdust/wood-waste.

### 3.2.1.1 Physical and chemical properties of a typical sawdust/wood-waste

Wood is a complex structure, it consists of polysaccharides which are made of smaller monosaccharides. These cells have different chemical compositions depending on their physiological need. Cells containing cellulose, hemicellulose and lignin are responsible for the strength and shape of the tree (Sjöström, 1993). The basic physical structure of wood is shown in Figure 3.1.

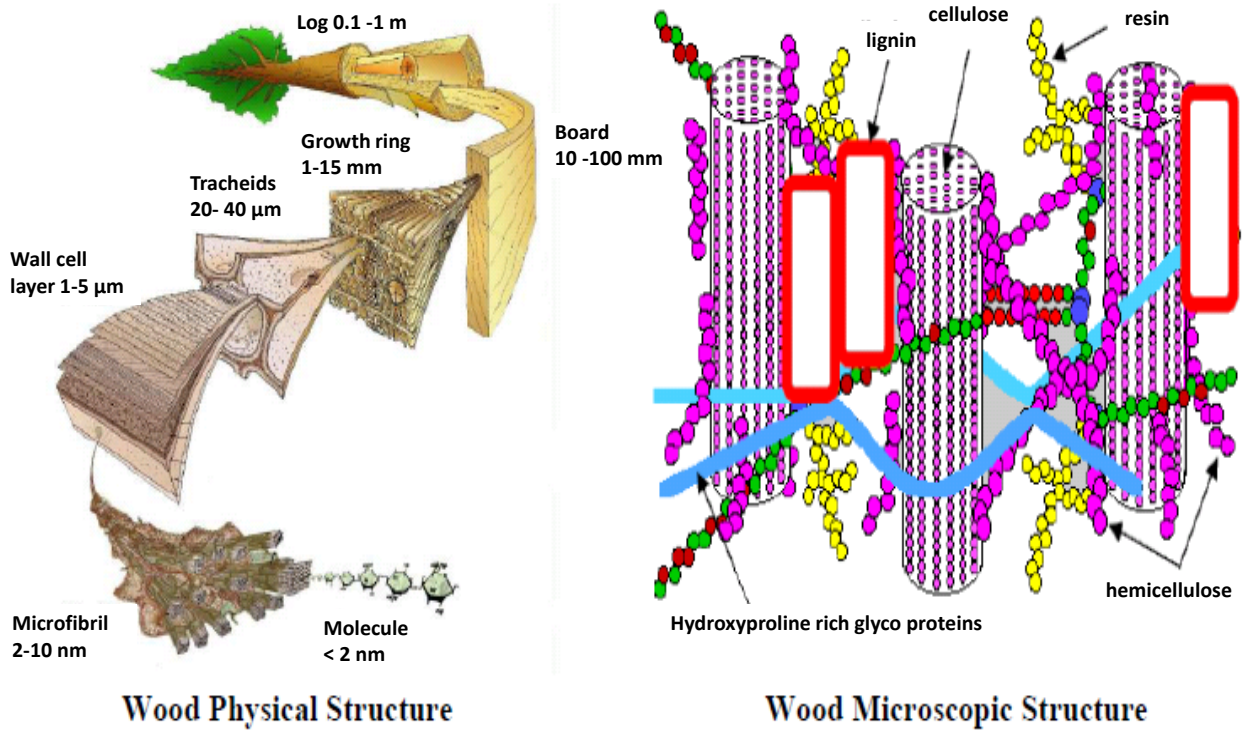


Figure 3.1 Diagrammatic wood molecular structures and a view of its microscopic appearance (Reed & McLaughlin, 2009).

Figure 3.1 shows the chemical components of typical sawdust. Pine (*Pinus.sp*) sawdust has a heating value of 15.01 MJ/kg, lower than coal at 31.8 MJ /kg, and is therefore not an efficient energy source. Therefore, alternatively sawdust can be added to soil as a carbonaceous material, where long term cropping has led to declining soil C concentrations (Shepherd et al., 2001). When wood-waste is applied to soil, soil N is immobilized and denitrified. The sawdust/wood-waste has readily available C, which can be easily consumed by microbes as shown Equation 3.1. (Robertson & Cherry, 1995).

$$5CH_2O + 4NO_3^- \rightarrow 5CO_2 + 2N_2 + 3H_2O + 4OH^- \quad \text{[Equation 3.1]}$$

Robertson and Cherry (1995) concluded that sawdust/wood-waste influenced the N cycle through the immobilization of N and denitrification.

Table 3.1. Characterization of pine sawdust (Chaula et al., 2014).

| **Proximate Analysis, dry basis (% w/w)** | | **Ash composition (% w/w)** | |
|---|---|---|---|
| Moisture | 16.44 | Sodium (Na) | 90.9 |
| Volatile Matter | 81.03 | Sulfur (S) | 3.56 |
| Fixed Carbon | 18.60 | Potassium (K) | 3.23 |
| Ash | 0.37 | Iron (Fe) | 0.76 |
| **Ultimate Analysis (% w/w)** | | Chlorine (Cl) | 0.40 |
| Carbon (C) | 48.62 | Phosphorus (P) | 0.38 |
| Hydrogen (H) | 5.79 | Chromium (Cr) | 0.35 |
| Oxygen (O) | 43.2 | Lead (Pb) | 0.30 |
| Nitrogen (N) | 2.39 | Copper (Cu) | 0.06 |
| H/C ratio | 0.12 | Zinc (Zn) | 0.04 |
| O/C ratio | 0.89 | Manganese (Mn) | 0.03 |

Most sorption-related research has been conducted with dry sawdust, and there are previous studies linking sorption of metal ions, inorganic N, dyes, and oils. (Harmayani & Anwar, 2012; Shukla et al., 2002). Sawdust waste has been used as a bulking agent with sewage sludge, before addition to soil, in an attempt to eliminate the negative properties (such as unstable mineral N) of the sewage (Banegas et al., 2007; Bugbee, 1999). However, sawdust has a poor water holding capacity and contains low amounts of plant nutrients (Trolove et al., 2005). This leads to a reduction in plant yields when sawdust is applied (Barney & Colt, 1991; Trolove & Reid, 2003). Trolove et al. (2005) also showed that sawdust cation exchange capacity (CEC) increased from 9 $cmol_c/kg$, to 94 $cmol_c/kg$ after 13 months when applied to soil. This potentially enhances N retention in the soil. Sorption of $NH_3$-N by sawdust may also improve N retention in soil (Hu et al., 2007).

Sawdust has also been identified as an excellent electron donor (Kim et al., 2003; Robertson & Cherry, 1995; Schipper & Vojvodic-Vukovic, 1998; Shukla et al., 2002), supporting denitrification and possible N immobilization. Kim et al. (2003) showed that

sawdust used in “bioretention” columns removed 95% of the $NO_3^-$ from synthetic storm water, compared to 6% in the control columns.

#### 3.2.1.2 Microbial properties and interaction with N

Robertson and Cherry (1995) conducted a field trial on denitrification in a septic field system using reactive porous media barriers. Two configurations of barriers (horizontal and vertical) were positioned below a conventional septic system. The reactive material consisted of sawdust (20%v/v), enhanced heterotrophic denitrification. During the one-year trial, there was a 60-100% reduction in $NO_3^-$. The authors estimated that about 1 kg of C was required for the denitrification of 1 kg $NO_3^-$-N, and the sawdust (slowly degradable C) incorporated in this trial could provide for 200 years of denitrification. Even if only 10% of the organic C were available for denitrification, this would last for about 20 years, the typical design life of a septic system.

Schipper and Vojvodic-Vukovic (2000) built an interception wall perpendicular to the shallow ground water flow mixing excavated soil with 40 $m^3$ of *P. radiata* sawdust. The denitrification rate was in the range of 0.6 -18.1 ng/$cm^3$/h, this accounted for the $NO_3^-$-N losses equal to 0.8 -12.8 ng N/$cm^3$/h from the ground water. The treatment wall removed $NO_3^-$ from groundwater for more than 2.5 years.

#### 3.2.1.3 Persistence or degradation in soil

Wood-waste longevity in the soil depends on the original plant species, part of the tree, original state of the wood-waste (wet or dry conditions and decomposition level), its coarseness, soil texture and temperature (Gholz et al., 2000). According to Barney and Colt (1991) the hardwoods (broadleaf trees) generally decompose more rapidly than softwoods (conifers) and that decomposition is accelerated by a high soil N environment. However, the wood of Scots pine has a high resin content, which makes it much more resistant to decay, and it can take several decades for a pine log to decompose fully. The C:N ratio of the ecosystem

strongly affects wood decomposition dynamics (Aber 1990). For example, a material with a lower C:N ratio would be more easily decomposed by microorganisms, being known as a more labile material (Reinertsen et al., 1984).

The persistence of wood-derived C in soil can be increased by pyrolysis of these organic wastes to biochar/charcoal. Conversion of biomass C to biochar leads to C sequestration (the stable fraction of C in biochar). The recovery of C is about 50% of the initial C compared to 3% remaining when the biomass is burnt or biological decomposition (<10–20% after 5–10 years) (Lehmann et al., 2006).

### 3.2.2 Biochar or charcoal

#### 3.2.2.1 Expected structure of biochar or charcoal

Biochar is the product of thermal degradation of organic materials in the absence of air (pyrolysis), and is distinguished from charcoal by its use as a soil amendment (Lehmann et al., 2011). It comprises a range of materials, from poly-aromatic carbon sheets or graphitic carbon, linked by covalent bonds, with other elements such as (hydrogen) H and (oxygen) O (Figure 3.2).

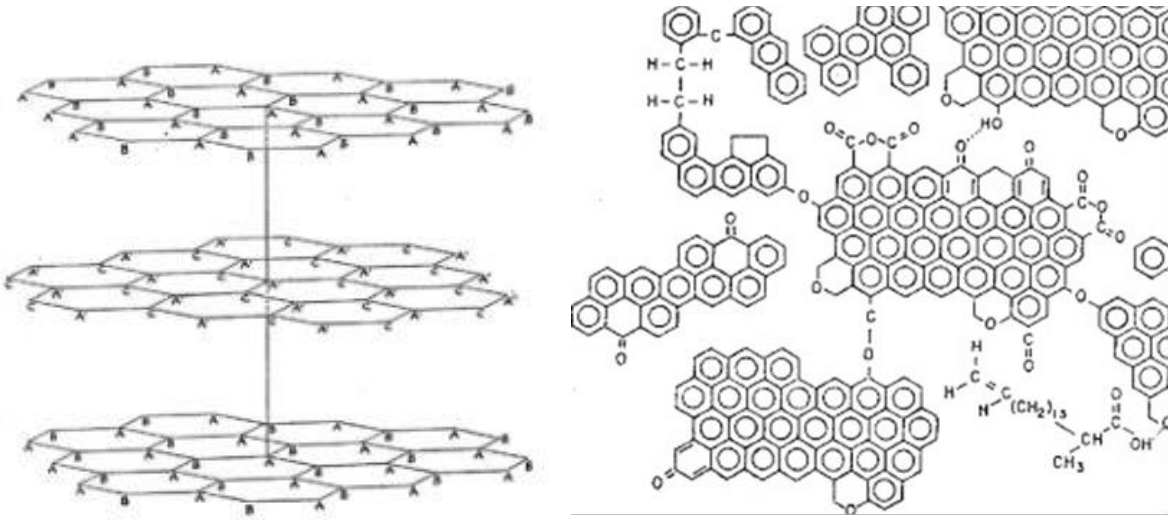

Figure 3-2 *Left:* First proven structure for graphite by J.D Bernal in 1924, cited by (Lehmann & Joseph, 2009), *Right:* Inter-linked covalent bond between the sheet.

### 3.2.2.2 Pyrolysis

Pyrolysis is one of the technologies used to produce energy from biomass (Bridgwater, 2003) (Figure 3.3). The heat and gases ($H_2$, CO, and $CH_4$) can be used to produce electricity, bio-oil or hydrogen for household uses (Lehmann (2007). These gases are also used in industrial processes, such as Fischer–Tropsch (CO as a precursor for diesel) and Haber–Bosch ($H_2$ as a precursor for atmospheric N fixation) (Sohi et al., 2010). The source (feedstock) for biochar production includes a wide range of materials, from parts of a tree (wood, bark, leaf, fruit skin or shells), to grasses, crop residues, animal residue and other biomass.

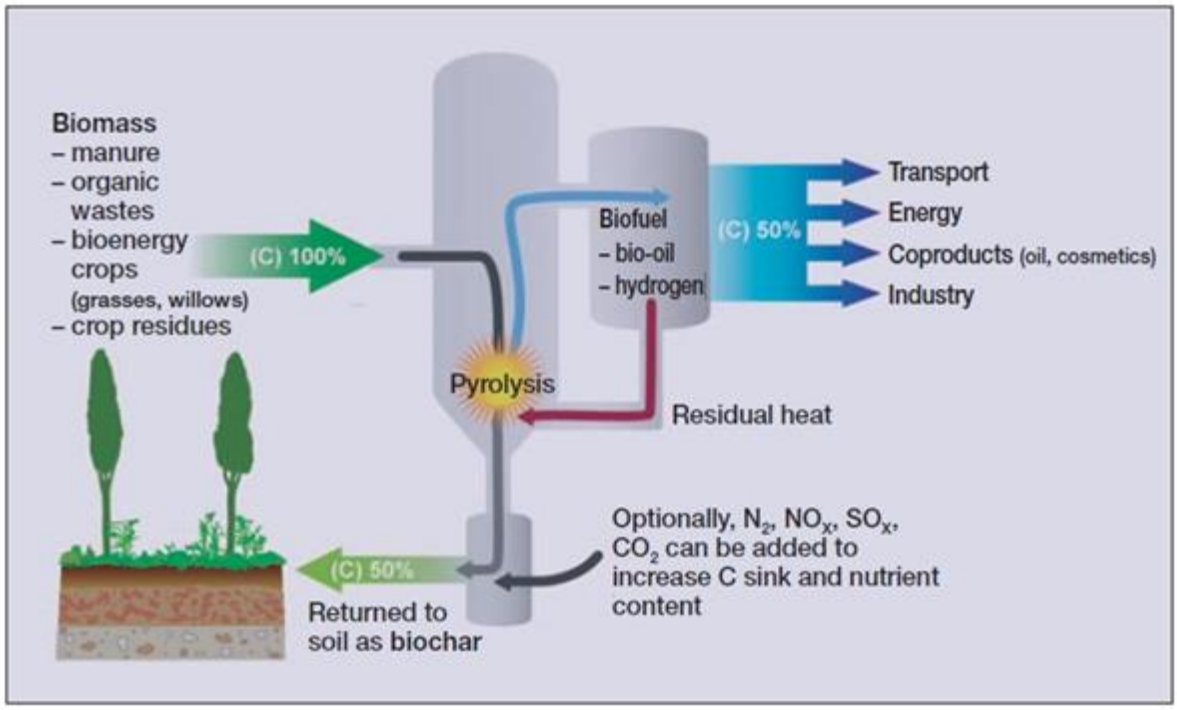


Figure 3-3 Concept of controlled low-temperature pyrolysis (400-500ºC) and production of bio-energy with biochar sequestration (Lehmann, 2007).

The physical and chemical characters of biochar depend on both feedstock and pyrolysis conditions (Gai et al., 2014). During pyrolysis, the oxygen environment is restricted to low or nil. High temperature pyrolysis (>700$^{o}$C) causes gasification, where the yield of biochar is reduced (complete ashing). Water in the biomass is lost through evaporation, while thermal decomposition generates volatile organic compounds.

Plant cells degrade at different temperatures; hemicellulose at between 200 -260$^{o}$C, cellulose between 240 -350$^{o}$C and lignin between 280 -500$^{o}$C (Sjöström, 1993). This thermal decomposition concept of wood is shown in Figure 3.4. Thermal Gravimetric Analysis (TGA) is a method of thermal analysis where changes in the physical and chemical properties of a material are measured as a function of increasing temperature. TGA is discussed further in Chapter 4.

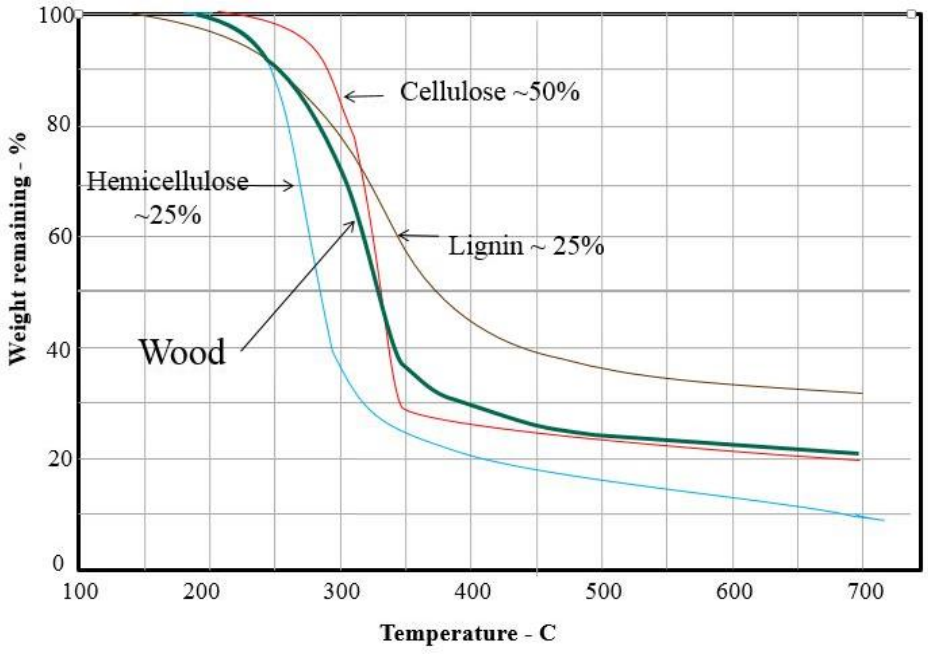


Figure 3-4. Pyrolysis of the wood biomass component by TGA (Reed & McLaughlin, 2009).

Table 3.2 shows the major components and their recovery during different pyrolysis conditions. Here, the proportion of biochar (solid) and syngas recovery decreases with pyrolysis rate but production of bio-oil increases.

Table 3.2. Pyrolysing processes and the fate of the feedstock: IEA (2007) and cited by Sohi et al. (2010).

| Process | Liquid (bio-oil) | Solid (biochar) (%) | Gas (syngas) (%) |
|---|---|---|---|
| *Fast pyrolysis*: Moderate temperature (~500 °C), short hot vapor residence time (<2 s) | 75% (25% water) | 12 | 13 |
| Intermediate pyrolysis: Low-moderate temperature, moderate hot vapor residence time | 50% (50% water) | 25 | 25 |
| *Slow pyrolysis:* Low-moderate temperature, long residence time | 30% (70% water) | 35 | 35 |
| *Gasification:* High temperature (>800 °C), long vapor residence time | 5% tar (5% water) | 10 | 85 |

### 3.2.2.3 Physical, chemical and microbial properties

Biochar was identified as a material suitable for C sequestration (Atkinson et al., 2010). Lehmann (2007) mentioned that this is a promising approach to lowering $CO_2$ in the atmosphere (as plants can fix $CO_2$), which is then used to produce biochar based on low-temperature pyrolysis. There are many studies on its use in waste management (Agblevor et al., 2010; Cao et al., 2009), composting with other waste materials, such as biosolids (Gartler et al., 2013; Knowles et al., 2011; Steiner et al., 2010), rebuilding degraded land (Robinson et al., 2011) and reducing green-house gas ($N_2O$ or $CH_4$) emissions (Liu et al., 2014; Sohi et al., 2010; Spokas et al., 2009; Steiner et al., 2010; Taghizadeh-Toosi et al., 2011; Yu et al., 2013; Zhang et al., 2010). There is interest in the use of biochar for the sorption of nutrients and contaminants from the soil/water and other industrial products (Asada et al., 2002; Spokas et al., 2009; Wang et al., 2010; Yu et al., 2009).

Biochar's physical, chemical, and biological properties are highly variable (Lehmann et al., 2011). There is considerable interest in biochar due its long persistence and its ability to retain cations better than other forms of soil organic matter. It potentially improves soil fertility by having the following properties:

- porosity
- functional groups on the surface
- surface area for sorption-desorption of ions
- Some biochars influence the pH of the soil by liming effect
- microbial pool on the char and persistence in the soil

Biochar can be activated to promote these characteristic properties, using physical activation methods e.g. steam activation (Azargohar & Dalai, 2008; Fan et al., 2004), water-nitrogen mixture gasification (uncatalyzed and iron-catalysed) (Rodriguezreinoso & Molinasabio, 1992), $CO_2$ (Koutcheiko et al., 2007) or chemical activation e.g. compound $ZnCl_2$ (Chen et al., 2002), co-precipitation of $Fe^{3+/}Fe^{2+}$ (Chen et al., 2011), concentrated $H_2SO_4$ acid (Mohan et al., 2004) and KOH (Azargohar & Dalai, 2008).

Figure 3.5 shows how pyrolysis conditions affect yield and chemical properties. Biochars manufactured at high temperatures (500-700$^{o}$C) contain mainly aromatic C (due to the effect of carbonization) and the CEC (up to a certain temperature), pH and surface area increase with temperature. At temperatures >600$^{o}$C the surface area can decline, due to shrinkage of micropores (Downie et al., 2009). The CEC plays an important role in the capacity of biochar to retain water, nutrients, gases and soluble organic compounds. The CEC is a function of the presence of hard ligand functional groups in the char such as carboxyl and phenolic groups (Carrier et al., 2012). Some biochars produced in pyrolysis result in high pH and high CEC chars which have a high liming effect in soil (Libra et al., 2011).

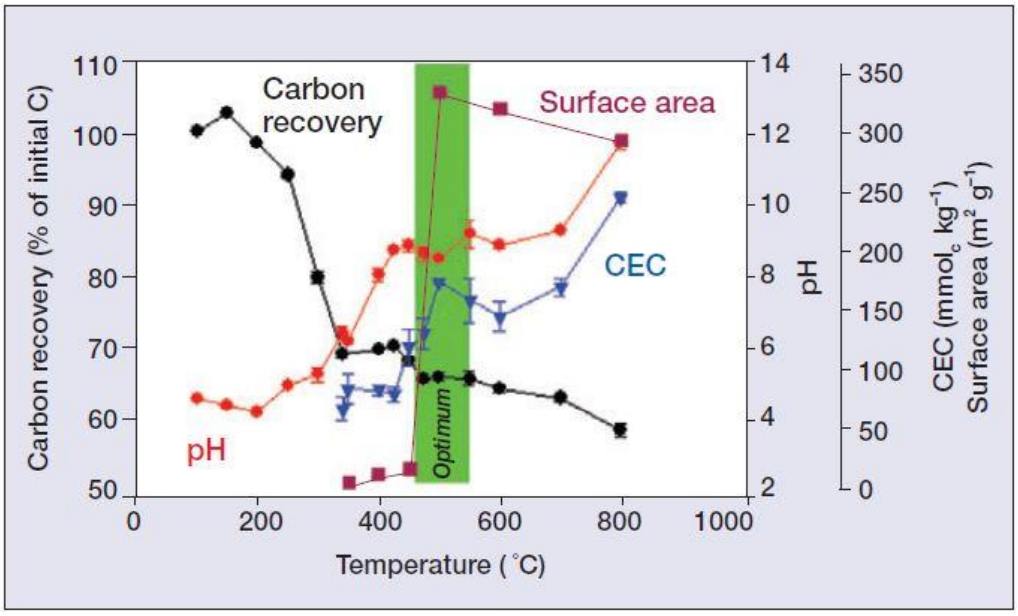


Figure 3-5. Factors affecting biochar properties, mainly pyrolysis conditions, temperature and C recovery, cation exchange capacity (CEC; measured at pH 7), pH, and surface area are shown here (Lehmann, 2007).

#### *3.2.2.3.1 Physical*

Naturally occurring biochar, resulting from forest fires, shows a basic graphite structure (Figure 3.2 left) however, manufactured biochars have a form that depends on the pyrolysis conditions and feedstock type. During pyrolysis, the external and internal surfaces of the biochar form, which is characteristic for each char and their pyrolysis conditions. The Brunauer Emmett and Teller (BET) method can be used to measure the surface area (Anderson et al., 2013). The surface area increases with the activation process during the pyrolysis, however, not all the pyrolysis includes activation (Carrier et al., 2012; Mohan et al., 2007).

#### 3.2.2.3.1.a Porosity and particle size of the char.

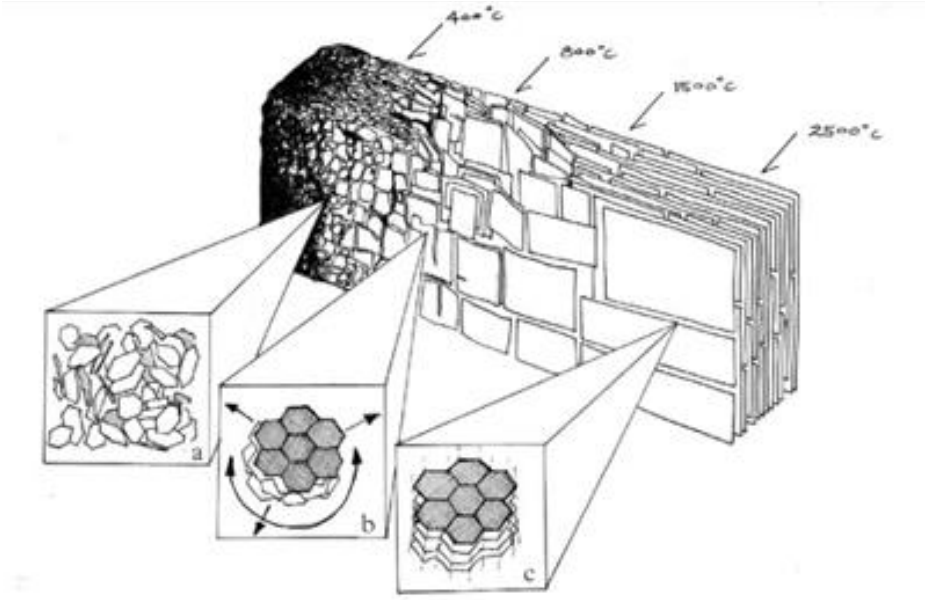


Figure 3-6. Diagrammatic structure of development of biochar with highest treatment temperature (HTT). (a) Increased amount of aromatic C, dis-ordered in amorphous mass, (b) conjugated aromatic C in sheets formation, (c) three dimension graphitic formation (Downie et al., 2009).

Downie et al. (2009) differentiated these pores as (i) micropores (internal diameter less than 2 nm), (ii) mesopores (2-50 nm), and macropores (>50 nm) (Figure 3-6) Macropores were responsible for the water holding (available to plant) property and aeration function of biochars, while micropores provide most of the surface area of biochar. Initially, they may be filled with tars, but during thermal decomposition, these micropores become accessible. Their number increases with the HTT (Highest Treatment Temperature) (600-750°C (Brown et al., 2006) and these are available for the sorption of ions.

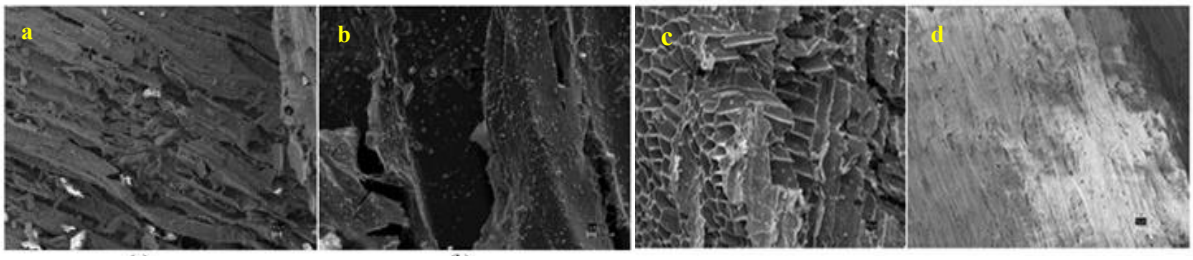


Figure 3-7. Scanning electron microscope images (2000 ×) of pine (*P. radiata*) with four different pyrolysis conditions. (a) at 300°C, no agitation (b) at 300°C, with agitation, (c) at 350°C, no agitation (d) at 500°C, no agitation [ PhD thesis, by A.Taghizadeh-Toosi (2011)].

Biochar particle size also depends on feedstock (it also depends on pre-processing and post-processing of the feedstock) and this in turn affects the quality and potential uses of biochar (Sohi et al., 2010). Particle size is bigger in the feedstock than the resultant biochar, due to shrinkage of the material during pyrolysis. Biochar manufactured from sawdust and wood chips have a different particle size than bulk woody materials. Initially, the ratio of exposed to total surface area of biochar will be affected by its particle size. The strength of low temperature biochar is greater than high temperature biochar, which is more brittle and breakable into fine fractions when incorporated into soil (Sohi et al., 2010).

McLaughlin et al. (2012) characterized pine wood biochar and studied the adsorption and absorption phenomenon. Biochar has an internal volume, typically characterized as porosity, which is filled by absorbate (e.g. gas or ions). The absorbent may swell as additional material is absorbed (Figure 3-8).

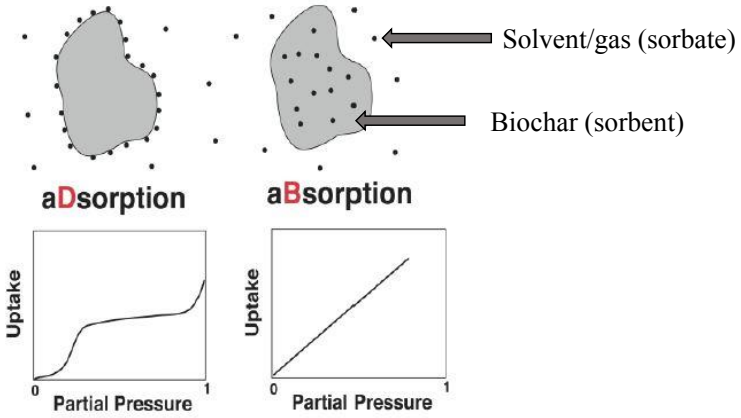


Figure 3-8. Characteristic shape of the isotherm relating the uptake to the partial pressure of the sorbate in the case of vapour phase sorption (adopted:(McLaughlin et al., 2012)).

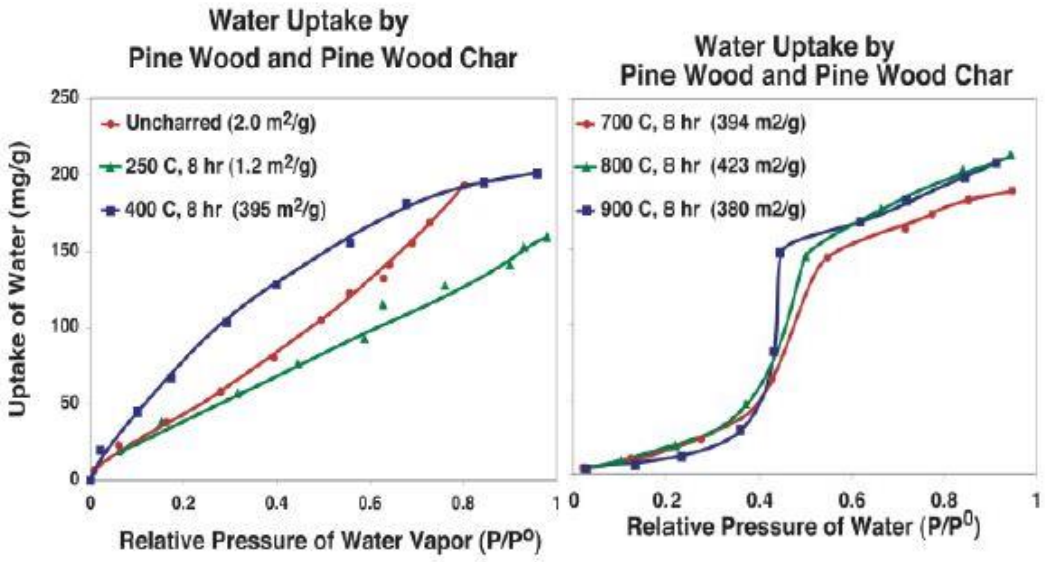


Figure 3-9. Water vapour isotherms of pine wood and pine wood char produced at different HTTs (McLaughlin et al., 2012).

Figure 3-9 clearly shows up to 400$^{o}$C absorption was dominant in pine wood biochar, on the other hand, above 700$^{o}$C adsorption was the dominating phenomenon. These results show a slight change in HTT could make biochar properties dramatically different and depends on its character.

#### 3.2.2.3.1.b Density

Two methods can be used to measure biochar density. Guo and Lua (1998), studied solid (true) density and the apparent (bulk) density of biochars manufactured at 400-900ºC. Solid density is the density on a molecular level, related to the degree of packing of the C structure. Bulk density is that of the material consisting of multiple particles and includes the macro porosity within each particle and the inter-particle voids. Often, an increase in solid density is accompanied by a decrease in apparent densities as porosity develops during pyrolysis. Solid density of biochar increases with increasing pyrolysis temperature and longer heating residence times (Downie et al., 2009). Guo and Lua (1998) showed that solid density increased up to 800ºC, while apparent density decreased. This was due to the increase in porosity (8.3 -24%) of the chars (Table 3.3). However, at 900ºC the apparent density of the char increased even though the porosity decreased, and this was attributed to the sintering effect (shrinkage of the pores).

Table 3.3 Densities and porosities of the chars prepared at different temperatures for various times (Guo & Lua, 1998).

| Pyrolysis temperature (ºC) | Retention time (h) | Solid density ($g/cm^3$) | Apparent density($g/cm^3$) | Porosity (%) |
|---|---|---|---|---|
| 400 | 3 | 1.57 | 1.44 | 8.3 |
| 500 | 3 | 1.60 | 1.40 | 12.5 |
| 600 | 3 | 1.63 | 1.35 | 17.2 |
| 700 | 3 | 1.64 | 1.32 | 19.5 |
| 800 | 3 | 1.67 | 1.27 | 24.0 |
| 900 | 3 | 1.69 | 1.31 | 22.5 |
| | | | | |
| 800 | 1 | 1.58 | 1.33 | 15.8 |
| 800 | 2 | 1.63 | 1.30 | 20.2 |
| 800 | 3 | 1.67 | 1.27 | 24.0 |
| 800 | 4 | 1.68 | 1.29 | 23.2 |

The correlation between feedstock bulk density and biochar bulk density is shown in Figure 3-10, where the effect of feedstock can be seen (Downie et al., 2009). The loss of volatile and condensable compounds during the pyrolyzation of biochars and the relative increase in

graphite form leads to the increase in solid density (or true density) of the biochars compared with their feedstock (Emmerich et al., 1987). Lower amounts of volatiles, which have lower molecular weights than fixed C, and lower ash contents result in higher solid density in biochars (cited by Downie et al. (2009).

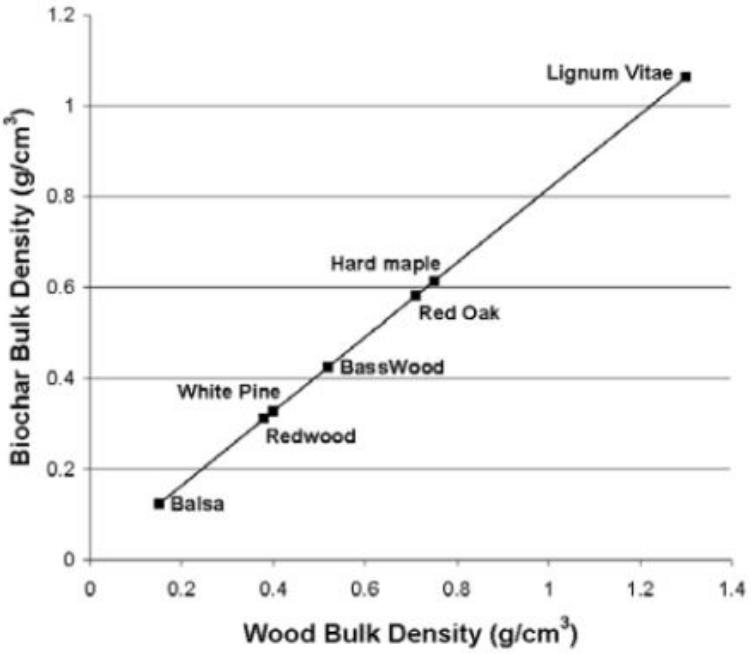


Figure 3-10. Bulk density of woody feed-stocks verses their resultant biochars (Downie et al., 2009).

#### *3.2.2.3.2 Microbial property of the biochar/Persistence in nature*

**3.2.2.3.2.a Microbial property**

Biochars have distinctive porous structures with different diameters. These porous structures provide more sorption area (to sorb solution/gases) for the biochar and help in sorption of heavy metal ions, inorganic ions, soluble gases like oxygen ($O_2$) and $CO_2$ and water. However, the porous spaces are also suitable habitats for soil microbes (bacteria and fungi) to grow, reproduce and colonize (Table 3.4) (Thies & Rillig, 2009).

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Table 3.4. Pore diameters in wood and bamboo biochar compared to the diameter of typical soil microbes (Thies & Rillig, 2009).

| | **Diameter (µm) range** |
|---|---|
| Bamboo biochar-pores | 0.001-1000 |
| Wood biochar | 10-3000 |
| Bacteria | 0.3-3 |
| Fungi | 2-80 |
| Protozoa | 7-30 |
| Nematodes | 3-30 |

If there is sufficient $O_2$ in these pores, then aerobic respiration will dominate in that microenvironment, while anaerobic respiration will dominate in low $O_2$ environments and the common end products formed are NO, $N_2O$, $N_2$, $NO_3^-$, $NH_3$, $H_2S$, $CH_4$ (Thies & Rillig, 2009). Anderson et al. (2014) showed some bacterial families (e.g *Bradyrhizobiaceae* and *Hyphomicrobiaceae*) were capable of using gases/nutrients such as $N_2$, $NO_3^-$, $NH_3$. They were also able to fix $N_2$ from the atmosphere using the $N_2$ fixation process. In their study, the microbial soil community did not change after two years. However, where biochar-amended soil was incorporated with ruminant urine patches, there was an increase in nitrifiers and denitrifiers, which influenced N fluxes. Dempster et al. (2012a) showed that the microbial C biomass significantly decreased and the microbial N biomass was unaltered, after application of biochar manufactured from Jarrah (*Eucalyptus marginata)* at a rate of 5-25 t/ha. They also showed that net N mineralization was higher in control soil, and decreased with the increased addition of biochar. Compared to bacteria, fungi are more tolerant of extremes of pH and temperature (Thies and Rillig (2009). These conditions influence the ratio of bacterial: fungal colonies in soils amended with biochar.

#### 3.2.2.3.2.b Persistence in nature

As organic matter decomposes, labile C is easily degraded (as in the microbial biomass) with a turnover of 1-5 years, however humic/organic C takes decades to decompose (Free et al., 2010). According to Winsley (2007), biochar is a highly stable and long-term form

of C sequestration overall, because charcoal is inert and resistant to biochemical breakdown. The *Terra preta* soils (it owes its name to its dark colour, caused by a high charcoal content) are up to several thousand years old. The average age of black C buried in deep-sea sediments was found to be up to 13 900 years, greater than the age of other organic C, such as humic substances. Charcoal from volcanic eruptions was dated back over 20 000 years (Winsley, 2007). Information shows that 'recalcitrant' carbon can be stored for many more years than its original source.

#### 3.2.2.4 Interaction with N

Biochar has the potential to alter the N cycle, via, (i) inhibiting N mineralization, (ii) influencing nitrification (iii) adsorbing $NH_4^+$ from the soil, (iv) immobilising either $NH_4^+$ or $NO_3^-$, (v) influencing $NO_3^-$ leaching, and (vi) influencing $N_2O$ emission.

Ammonium sorption by a biochar is related to the CEC of that biochar. CEC values are highly dependent on pyrolysis conditions and feedstock type (described in Figure 3-5) (Lehmann, 2007). Cheng et al. (2006) studied oxidation of biochar by biotic and abiotic processes. They incubated biochar in soil at 30$^o$C and 70$^o$C for a duration of 4 months with and without microbial inoculation. In the abiotic environment, biochar pH decreased from 5.4 to 5.2 and 3.4 respectively and CEC increased by 53% and 538% respectively. This increase was due to the increased number of carboxylic functional groups. At 70$^o$C, oxidation penetrated through the biochar into the pore surfaces, at the same time the 30$^o$C oxidised the outer surface of the biochar.

Rodrigues et al. (2007) studied $NH_3$ sorption on a commercially activated C, manufactured from coconut shell. They used between 600-2400 mg/kg concentrations of $NH_3$, and studied the sorption capacity at three different temperatures. The results were 0.6 to 1.8, 0.2 to 0.7, and 0.15 to 0.35 mg $NH_3$/g carbon at 40, 80 and 120$^o$C respectively.

Few studies have specifically examined $NO_3^-$ sorption or leaching in biochar. Chintala et al. (2013) studied $NO_3^-$ sorption by fast pyrolysis (at 650$^oC$) using biochar from corn stover (*Zea mays* L.), Ponderosa pine wood chips (*Pinus ponderosa* Lawson and C. Lawson), and switchgrass (*Panicum virgatum*), showed that acid (concentrated HCl) activated pine biochar increased $NO_3^-$ sorption by 440%. Knowles et al. (2011) showed a 50% reduction in $NO_3^-$ leaching, when pine biochar (102 t/ha) was incorporated with biosolids-amended soil compared to biosolids alone treatment in a field lysimeter trial.

Toxic or nitrification inhibiting compounds in biochar and also the level of biochar weathering and residence time in the soil clearly influence N cycling (Clough and Condron (2010). Some toxic compounds are condensed during biochar pyrolyzation e.g. polycyclic aromatic hydrocarbons, cresols, xylenols, formaldehyde, acrolein, and other toxic carbonyl compounds that can have bactericidal or fungicidal activity (Painter, 1998). However, Ogawa (1994) showed that such toxic chemicals can provide a C energy source for certain types of microbes. These chemicals eventually disappear with weathering of biochar in soil, at the same time CEC increases.

Steiner et al. (2008) studied the retention of N in a central Amazonian trial. Charcoal derived from secondary forest wood was incorporated (at a rate of 11 t/ha) in soil. They used $^{15}N$ added ammonium fertilizer and grew sorghum (*Sorghum bicolor* L. Moench). Their results showed higher N retention by organic amendments (charcoal) compared to mineral fertilizer plots. They concluded that N retention was either by increased CEC or enhanced immobilization by the microbial biomass.

## 3.3 Lignite

The chemical composition of lignite is not defined. Its properties vary by site and formation history of the lignite and the process occurs over geological time frames. Wood buried in soil decomposes via oxidation, with the formation of hydrogen, carbonic acid, carbonic oxide, water, petroleum. With time, pressure and heat, this turns in to the darker and denser substance called lignite (Figure 3-11). Lignite occupies an intermediate position between peat (Bowen & Irwin, 2008; Zein El-Abedine, 1982) and hard bituminous coal (Figure 3-12). In favourable conditions, peat turns into lignite, and lignite into coal or anthracite. There is limited research into lignite or brown coal with respect to inorganic N sorption.

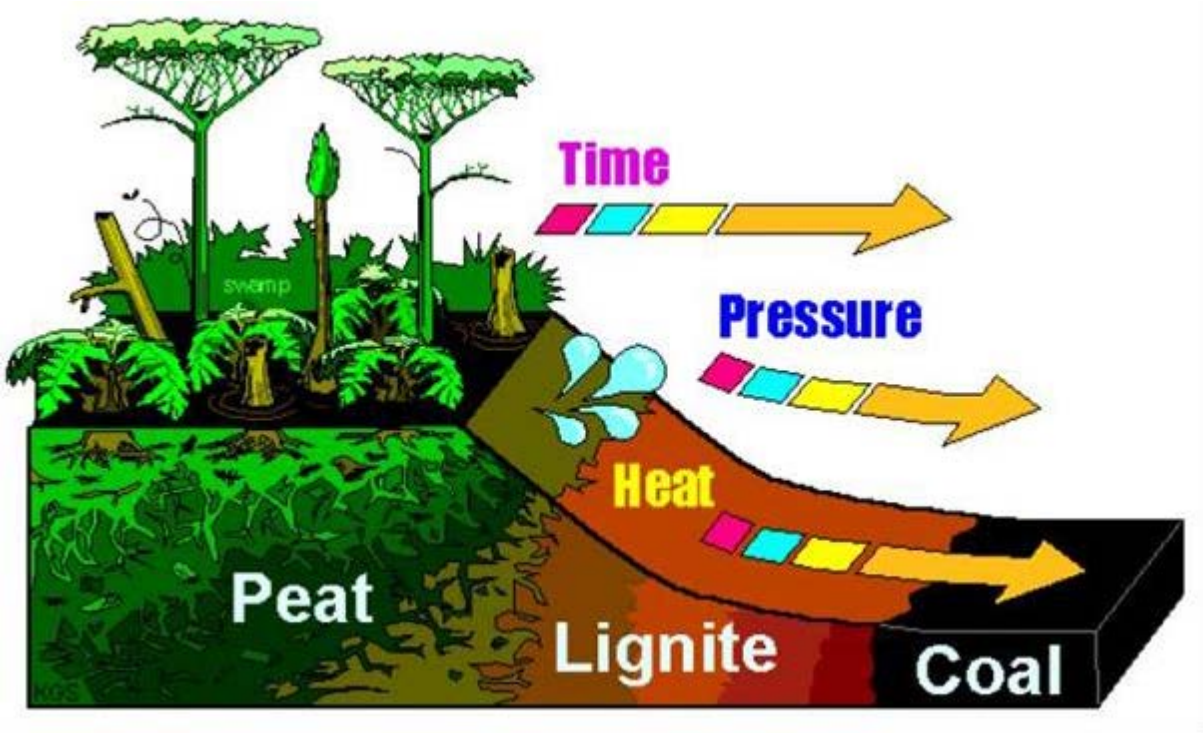


Figure 3-11. Geological processes in the formation of peat, lignite and coal (Bowen & Irwin, 2008).

### 3.3.1 Physical and chemical properties

Lignite is a low-grade fossil fuel, with a high moisture content (up to 70% by weight) (Bowen & Irwin, 2008). Therefore, it needs high energy to burn and releases large amounts of

$CO_2$ and other pollutants. The calorific value is between 7.8 to 10.5 MJ/kg, half that of firewood and providing three times less fuel capacity than of hard coal (27-33 MJ/kg) in power generation. Lignite is dark brown or black in colour when moist, and light brown when dry. Its density falls in the range of 1.0–1.35 g/cm$^3$ (Pehlivan & Arslan, 2006).

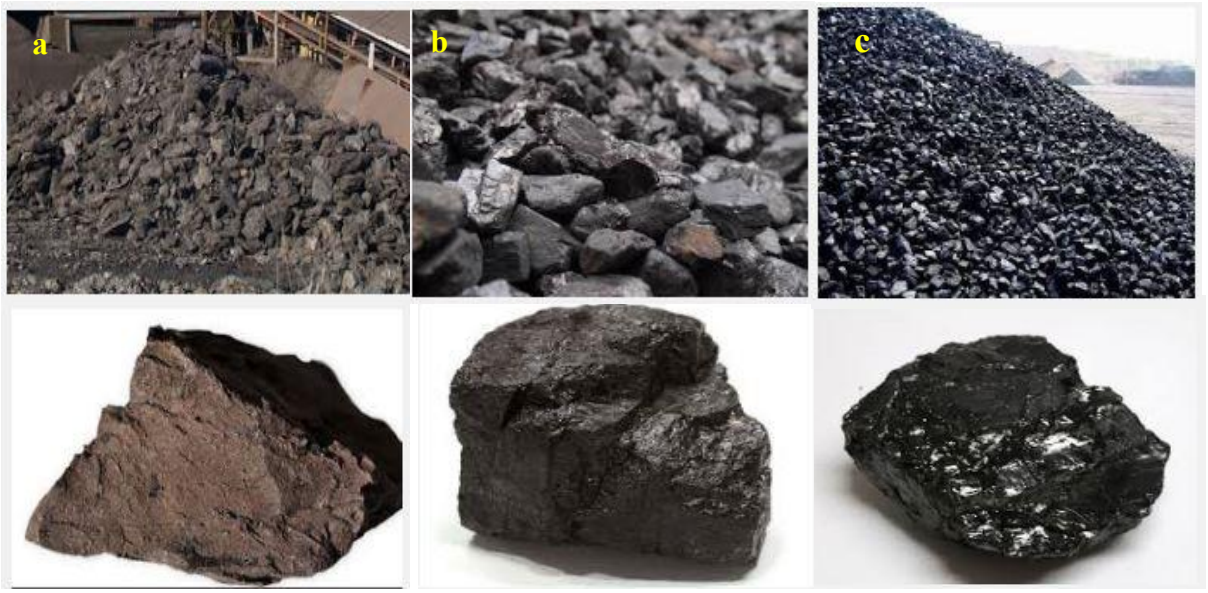


Figure 3-12. Pile of lignite (a), bituminous coal (b), anthracite coal (c), and the appearance of individual particles (Bowen & Irwin, 2008).

Physical properties vary for each stage of coal formation (peat, high grade coal via lignite). This is mostly controlled by (i) moisture, (ii) volatile content, and (iii) C content (Table 3.5). While no precise chemical formulae for coals can be given, the approximate empirical formula comprising bituminous coal is $C_{137}H_{97}O_9NS$, for high-grade anthracite $C_{240}H_{90}O_4NS$, and lignite $C_{270}H_{240}N_3S_1O_{90}$. Anthracite is a dense, hard rock, jet-black in colour and with a metallic lustre (Figure 3-12). It contains 86-98% C by weight. Volatile matter decreases as the coal rank increases, but low rank coal contains a higher percentage of hydrogen, oxygen and N whereas high-rank coal contains pure C up to 95% (Bowen & Irwin, 2008; Kabe et al., 2004).

Table 3.5. Properties of four different coals (Bowen & Irwin, 2008).

| % weight | Anthracite | Bituminous | Sub- Bituminous | Lignite |
|---|---|---|---|---|
| Heat Content (Btu/lb) | 13,000-15,000 | 11,000-15,000 | 8,500-13,000 | 4,000-8,300 |
| Moisture | < 15% | 2 - 15% | 10 - 45% | 30 - 60% |
| Fixed Carbon | 85 - 98% | 45 - 85% | 35 - 45% | 25 - 35% |
| Ash | 10 - 20% | 3 - 12% | ≤ 10% | 10 - 50% |
| Sulphur | 0.6 - 0.8% | 0.7 – 4.0% | < 2% | 0.4 – 1.0% |
| Chlorine (ppm) | 340 ± 40ppm | 340 ± ppm | 120 ± 20ppm | 120 ± 20ppm |

Btu/lb British thermal unit/pound.

### 3.3.2 Lignite as a soil amendment

The negative properties of lignite would not be an issue if used for non-energy or non-fuel applications. Many studies have shown that lignite can be an effective soil amendment because of its high Humic Acid (HA) content (Janos et al., 2011; Kucerik et al., 2003), and soil conditioning properties (Chassapis et al., 2009; Doskocil et al., 2015; Pehlivan & Arslan, 2007; Song & Schobert, 1996). Tahir et al. (2011) studied plant growth in different soils amended with lignite–derived HA. They incorporated rates of 30, 60 and 90 mg/kg HA, the highest height and shoot fresh and dry weights were observed with 60 mg/kg treatment compared to control (no HA added). The water and nutrient holding capacity of the lignite improved degraded soil (Richards et al., 1986).

Lignite can reduce or remove metallic ions/heavy metals from contaminated soils (Budaeva et al., 2006; Domańska & Smolinska, 2012; Doskocil & Pekar, 2012; Karczewska et al., 1996) and remove radionuclides and potentially toxic metals from waste water treatments/ polluted water (Mizera et al., 2007; Mohan & Chander, 2006). Recent research shows lignite can reduce plant uptake of Cd and therefore may be an important amendment to New Zealand pastures (Simmler et al., 2013). Pehlivan et al. (2004) studied adsorption and desorption of Cu, Pb, Cd, Ni and Zn on a few Turkish lignites. They showed that sorption increased with pH, up to a certain value (2.7 -5.7). They used a reversibility technique for the sorption (soaked in a metal solution and used buffer solution to recover the metal). Binding was only 5 and 30%

reversible, indicating that ion exchange was not a dominating adsorption mechanism and hypothesised the size, shape of the cavity in the lignite structure and naturally occurring functional groups influenced the metal sorption and desorption. The authors concluded that lignite is therefore an inexpensive sorbent for the heavy metal ion.

Opinion is divided over lignite use as a soil amendment, with environmentalists claiming it harms both air and soil (Figure 3-13). Lignite can release unwanted chemicals such as aromatic hydrocarbons (Fabianska & Kurkiewicz, 2013), and some water soluble organic trace components (Peuravuori et al., 2006). Janos et al. (2011) found a type of young brown coal contained low concentrations of dangerous radionuclides, heavy metals and potentially hazardous elements but suggested the levels did not significantly exceed average values present in the earth's crust.


Figure 3-13. Protesters campaign against lignite mining in NZ (http://www.stuff.co.nz/southland-times/news/7010403/Anti-lignite-mining-billboard-put-up).

### 3.3.3 Cation exchange property

Lignite is known for its high concentration of oxygen-containing functional groups (Figure 3.14). These functional groups allow the lignite to remove cations from solution via ion exchange.

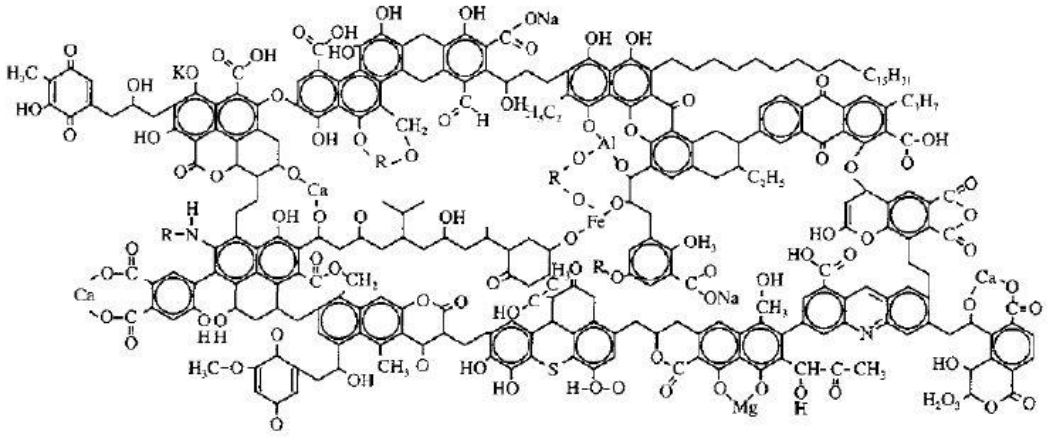

Figure 3-14. Diagrammatic chemical structure of a lignite (Kabe et al., 2004).

Skodras et al. (2014) studied the CEC of low rank Greek lignite and chars and identified two different CEC sites in both. The first type was pH independent; they called it permanent CEC, primarily derived from inorganic sites. They used a potentiometric titration method to measure the changes in CEC with pH variation (Figure 3-15).

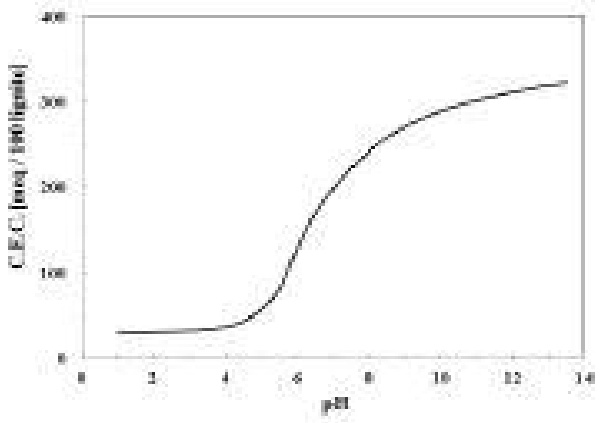


Figure 3-15. Variation of the CEC of lignite with the solution pH, obtained by titration with 0.1M NaOH (Kabe et al., 2004).

The second type of CEC was pH dependent and they called this variable CEC, derived from the organic matter in the lignite. Dissociation of carboxylic groups was directly linked to the oxygen content of the lignite. Greek lignite showed a CEC maximum of 330 $cmol_c/kg$. Others showed CECs of 20-70 $cmol_c/kg$ (Janos et al., 2011), and 44.8 $cmol_c/kg$ (Simmler et al., 2013).

The effect of lignite soil amendments on the N cycle is unknown, but two groups have examined the effect of modified lignite on the sorption of inorganic N. Khan et al. (2011) showed nitrate removal by a chemically modified lignite. They studied the pH of the solution and contact time for sorption (30 min) and the optimum chemical requirement to maximize sorption by lignite. Budaeva et al. (2006) studied ammonium ion sorption from wastewater by air plasma modified lignite; the modified lignite sorbed 23.2 g $NH_4^+/kg$ compared to the unmodified lignite, which sorbed just9 g $NH_4^+/kg$.

Kwiatkowska et al. (2008) found that seven years after application, soil amended with lignite had a higher C content, slightly higher N content and a higher C:N ratio than control soil. The C:N ratio has a critical influence on N mobility within soil.

### 3.3.4 Role of "black urea"

Among the current nitrogen management, urease inhibitors, nitrification inhibitors and impervious coatings have been utilised with some success. Black urea is carbon- coated urea, which is speculated to influence by increasing microbial activity and exchange capacity around the granule, resulting in the N being held in the cation and organic forms longer, reducing losses and improving N uptake (Advanced Nutrients, 2015). This is widely used by farms and many field trails were conducted in Australia (unpublished research so far). It is coated urea granules (Figure 3-16) and its composition is 46% N and 21% C. The coating can be any kind of organic compound which includes HA, fulvic acid, ulmic acid, amino acids, melanins,

peptides, polysaccharides, vitamins and minerals (Advanced Nutrients, 2015). These bind to urea and allow it to release the nutrient slowly and black urea is categorised as a slow-release fertilizer (ARTH, 2009). Humic acid is one of the main components of the coating material, and is high in lignite low rank coal. Lignite could be a potential candidate as a coating material, but further studies are required.

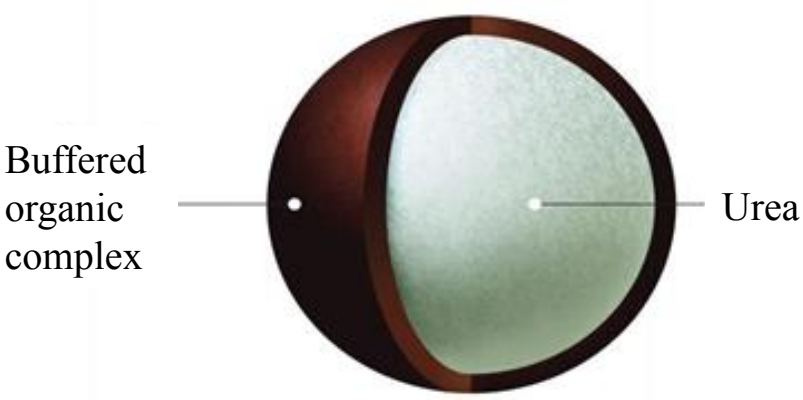


Figure 3-16. Coated urea granule (*Black Urea*, 2015).

There is no scientific evidence so far published relating to "black urea". To my knowledge, only one study was published by van Vuuren and Claassens (2009) in South Africa. Their greenhouse pot trail used "black urea" and other sources as an N fertilizer to grow maize. "Black urea" increased plant yield by 46%, compared to standard urea. Nitrogen loss and the effect of black urea on N loss via emission or leaching was not studied. They suggested that black urea would be best suited to grain crops, as well as sugar, fruit and vegetables. They referred to another unpublished field trial conducted in Australia with "black urea", which also out performed urea by 20-30%. There is no information available on the outcome of black urea application on grazed pasture.

### 3.3.5 Microbial propeties of lignite and the interaction with N

It has yet to be determined whether lignite has a positive effect on nitrifying and denitrifying bacteria in the soil. Equally unclear is whether lignite will provide refuge for soil microbes. The highly porous nature of lignite is similar to that of another carbonaceous amendment (e.g. biochar) (Kabe et al., 2004). However, according to Kabe et al. (2004), some fungi and bacteria (mostly aerobic) can degrade coal e.g *Actinomycetes,* yeasts, mould and lignin-degrading fungi have the ability to depolymerize coal matter to convert into low-molecular matters.

Dong et al. (2009) showed that soil amended with urea, with the addition of lignite HA, could buffer the change in microbial community composition and numbers, as well as the ammonia oxidising bacterial population size and potential nitrification, by reducing the urea to ammonium hydrolysis rate through the inhibition of urease.

#### 3.3.5.1 Interaction with N

Few publications relating to lignite coal and inorganic N sorption/leaching exist, while there are numerous studies relating lignite to heavy metal sorption. Lapcikova and Lapcik (2006) studied ammonium sorption from wastewater by a treated South Moravian lignite. Both the treated and untreated lignite (each 100g) showed affinity towards $NH_4^+$ (initial concentration was 150 mg/L), at 23 g $NH_4^+$/kg and 9 g $NH_4^+$/kg respectively. Using their adsorption isotherm, they predicted that adsorption was due to both chemical (27%) and physical (73%) processes. They suggested the use of lignite as a sorption material for $NH_4^+$ in industrial-scale wastewater treatment.

Hao et al. (2007) studied a commercially available lignite extract (97% water, 3% dry matter, denoted as LC) in gas emission in a cattle feedlot manure. They used 4 groups, each included 20 steers (randomly selected). The control group animals were fed with barley silage, while the other three groups received barley silage sprayed with 0.5, 1.0 and 2.0 L of LC/ t of

dry matter (DM). Manure samples were collected daily from Day 25 up to Day 150. The manure collected from the LC-spiked group showed low pH and dissolved $NH_3 + NH_4^+$ content in manure collected after 25 and 53 days of the experiment, and had significantly reduced $NH_3$ emission during this time. The values for samples collected on Day 25 were 3166 mg/kg (control) to 275 mg/kg of $NH_3$-N and 13287 mg/kg (control) to 4289 mg/kg of $NH_4^+$-N from the highest LC application. A similar effect was found on samples collected on the 53$^{rd}$ day, however; later days did not show any significant difference. They suggested that the lower manure pH, $NH_4^+$ content and $NH_3$ emission at early sampling dates indicated that LC could play a role in reducing gaseous ammonia N emissions to the atmosphere.

Vassileva et al. (2008) studied $NH_4^+$ removal from aqueous solution by two types of lignites, one from Chukurovo deposits in Bulgaria, and another commercially available. They used a different technique (treated with $HNO_3$, $H_2O_2$ and moist air) to activate both lignites. The initial $NH_4^+$ concentration was 35–280mg/L and the agitation/contact time was 2 hr. Lignites were activated by $HNO_3$ showed $NH_4^+$ sorption of 29 and 28mg/g from the commercial lignite and Bulgarian lignite respectively.

# Chapter 4: Characterization of biosolids and carbonaceous amendments used in this study

## 4.1 Materials

### 4.1.1 Introduction

Biosolids and the carbonaceous amendments used in this study are heterogeneous mixtures based on a matrix of organic macromolecules (Chassapis et al., 2009; Knicker, 2010; Singh & Agrawal, 2008). These materials have a diverse range of properties, depending on their provenance, level of treatment, and age (Chapter 2).

Clearly, it is impossible to measure all the permutations of biosolids mixed with carbonaceous amendments. To make any results relevant to scenarios other than the ones tested, the properties of the materials must be compared with other materials. Low cost carbonaceous materials are the key to this research and they were chosen for New Zealand conditions.

One of the carbonaceous materials selected for this research was biochar. Biochar is a rapidly-growing area of scientific research, especially for agronomic use (Kulyk, 2012), soil rehabilitation or soil quality improvement (Scharenbroch et al., 2013), mitigating environmental pollution (Ippolito et al., 2011) and greenhouse gas mitigation (Felber et al., 2014). However, the readily available feedstock for biochar pyrolyzation may differ in each country. Common examples include rice husk (Masulili et al., 2010) and rice straw char (common in many Asian countries), waste from tea plantations (Rajapaksha et al., 2014), coconut products (shells, husk, kernel waste) (Shenbagavalli & Mahimairaja, 2012), palm tree waste, waste from rubber plantations (Dharmakeerthi et al., 2012; Ghani et al., 2013) and sugar cane bagasse (Carrier et al., 2012). Sugar cane bagasse is a common feedstock in African countries, especially South Africa (Carrier et al., 2012). In Europe, biochar is commonly made

from corn or wheat stover switchgrass (Enders et al., 2012), eucalyptus (Zhang et al., 2015). Wood-waste is another possible waste material. The availability of wood-waste can also differ by region or country. Pine plantations are abundant in New Zealand, Australia, around Europe, and in the USA. The other widely available carbon rich material is low-grade coal called lignite. While many countries possess deposits of lignite and/or coal (see Chapter 3 for details), other countries do not e.g. Sri Lanka. Therefore, lignite availability is restricted to coal producing countries. Currently, lignite is used mainly for power/energy production in those lignite-producing countries. Therefore, if this research uncovers any significant findings regarding lignite and mineral N retention, it could open-up a new area of lignite research.

The aim of this study was to determine the physical and chemical properties of biosolids (Chapter 1 & 2) from the Kaikōura wastewater treatment plant (WTP), lignites from mines at New Value, Spring Creek (lignite Charleston) and Stockton (lignite Millerton), as well as a range of *P. radiata* biochars and sawdust (Chapter 3), and compare these properties with those of published materials. Furthermore, I sought to elucidate how the materials used in this thesis may differ in their ability to mitigate nitrate leaching from biosolids.

## 4.2 Material collection

### 4.2.1 Biosolids

Biosolids were obtained from the Kaikōura Regional treatment works (Figure 4-1: 42°21′45.30″S 173° 41′21.14″E), New Zealand. The initial treatment consisted of sedimentation and anaerobic digestion in settlement ponds (6-8 months) and then mound storage (over 25 years), whence the biosolids used for this experiment were obtained.


Figure 4-1. Kaikōura TP showing the sewage settlement pond and storage mounds (Google Earth).

Some 150 kg of biosolids were sampled from the WTP storage pile, sampling occurred at eight locations across the pile to obtain a representative sample. Studies by Knowles *et al*., (2011), Robinson *et al*., (2011), Simmler *et.al*., (2013) and Gartler *et al*., (2013) also sourced their biosolids from the Kaikōura WTP.

Figure 4-2. *Left to Right*- Kaikōura Regional treatment settlement pond (in the background); sand pit; sewage sludge/biosolids sampling site.

The collected biosolids were then homogenized in a concrete mixer and subsequently sieved to a grain size of <20 mm (nylon sieve). A sub-sample was collected and sieved to a grain size of <2 mm (nylon sieve). This was then air dried, collected and sealed in a plastic bag and stored in a refrigerator for future experiments.

### 4.2.2 Sawdust/wood-waste

All experiments used sawdust/wood-waste from *P. radiata* trees, which is subsequently referred to as "pine" in the text. Untreated sawdust was obtained from a local sawmill (SRS, Shands Road Sawmills Ltd), located in Canterbury, New Zealand. Forest wood-waste was collected from a pine plantation after logging (Figure 4-3). Wood-waste was then hand-cleaned by removing the small stems and leaves and dried overnight in a 60$^{o}$C oven. Biochar details are given in the sub-section 4.3.1.

Figure 4-3. Pine wood-waste generated from logging operations, McLeans Island Forest, Canterbury (Photograph by Brett Robinson).

### 4.2.3 Lignite

Three types of powdered lignites were provided by Solid Energy New Zealand Ltd. The New Vale lignite (NV particle size <200 μm), a low calorific value lignite, was sourced from an opencast mine in Southland, New Zealand, (Figure 4-4:46°08′58.25″S 168°45′09.38″E). Charleston lignite (particle size 1-2 mm) was sourced from the Charleston underground mine near Charleston, West Coast, New Zealand (Figure 4-4:*R*: 41°54′51.74″S 171°25′58.13″E), and the Millerton lignite (particle size 0.5 mm<2 mm), was sourced from the Millerton section of the Stockton opencast mine on the West Coast, New Zealand (Figure 4-4:*L*:41°39′47.41″S 171°51′55.51″E).

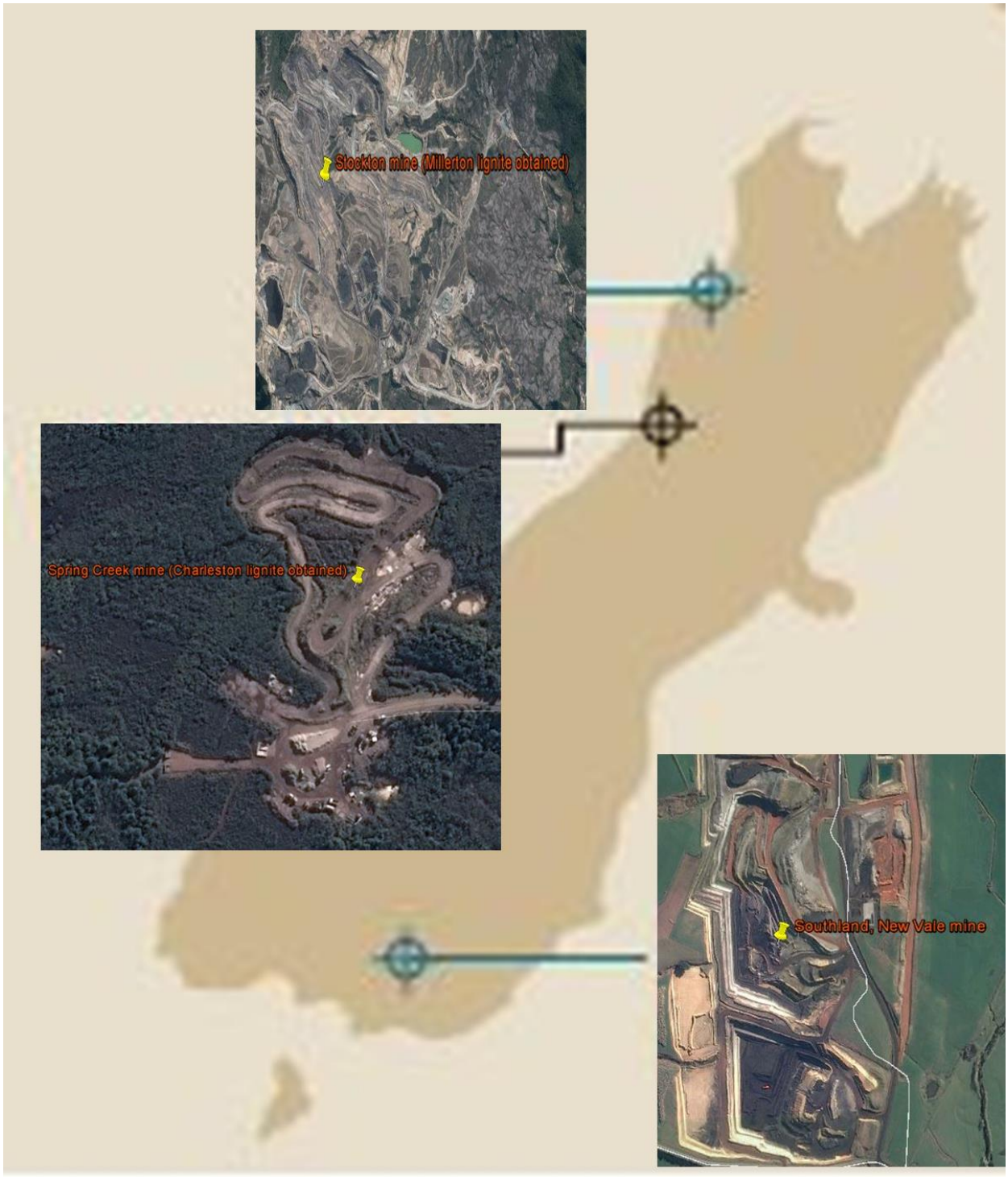


Figure 4-4 *Top:* Stockton opencast mine, West Coast, where Millerton lignite was obtained; *Middle:* Spring Creek underground mine, West coast, where Charleston lignite was obtained *Bottom:* Southland's New Vale mine is an opencast mine producing NV lignite (Google Earth).

## 4.3 Methods

### 4.3.1 Pyrolysis of biochars

#### 4.3.1.1 High temperature biochars (400°C and 550°C)

Pyrolysis was conducted under the supervision of Associate Professor Marta Camps Arbestain at the New Zealand Biochar Science Research Centre, Institute of Agriculture and Environment, Massey University, Palmerton North, New Zealand. The pyrolyzer was equipped with a 5 L rotating kiln (Figure 4-5), used liquefied petroleum gas (LPG) as the heating source (Pereira Calvelo et al., 2011) and an inlet to inject water for the steam activation. The pine wood-waste (200 g) was pyrolyzed at 400°C and 550°C with and without steam activation. For steam activation water was injected by pump into the pyrolysis chamber at a rate of 4 mL/min which had an airflow of 10 L/min (Figure 4-6).

Figure 4-5. *Left*-Setting-up the pyrolyzer; *Right*- During the pyrolysis, waste crude tar was collected in a two-necked round bottom flask.

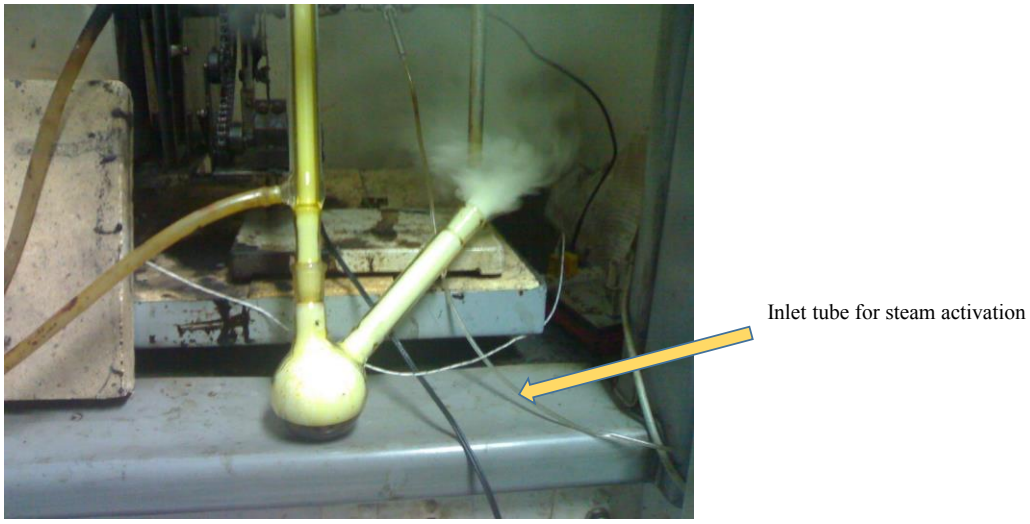


Figure 4-6. Close up of crude tar flask and inlet for steam activation (arrow).

The 400°C activated and 400°C non-activated biochar reached the target temperature at a rate of 38°C/min, and the 550°C activated and 550°C non-activated biochar reached the target temperature at a rate of 46°C/min. Each biochar was held for 10 min at the target temperature, during which time steam activation was applied. The 400°C biochars had an average recovery of 32.5% while the 550°C biochars had a 24.9% recovery (Figure 4-7). After cooling, the wood-waste biochars were crushed and sieved to a grain size <4 mm.

Figure 4-7. Pine wood-waste (left) and biochar pyrolyzed at 400°C with steam activation (right). NB- There was no distinguishable visual difference between steam activation and non-activated.

#### 4.3.1.2 Low temperature biochars (350°C)

Low temperature (350°C) biochars were manufactured using a muffle furnace (Zhang et al., 2015) at Lincoln University, Canterbury, New Zealand (Figure 4-8).

Figure 4-8. Furnace equipped with a thermocouple and exhaust ventilator.

Pine wood-waste (200 g) was weighed into steel containers equipped with a fine metal mesh at the bottom to hold the feedstock and covered with aluminium foil to restrict the available oxygen. The temperature was monitored using a thermocouple to ensure the temperature of the material was maintained at 350°C. Biochars were manufactured with pyrolysis times of 3 hr and 12 hr at the target temperature. The target temperature, 350°C, was reached at the rate of 16°C/min. The 350°C pine biochars prepared at the 3 hr period had a 49% of DM yield and the 12 hr biochar an average of 42% recovery (Figure 4-9). All these biochar materials were sieved to obtain a grain size of <4 mm.

Figure 4-9. Pine sawdust (left) and biochar manufactured at 350°C (3hr) (right).

Highest Treatment Temperature (HTT) influenced biochar texture and recovery. Biochars pyrolyzed using the furnace at 350°C were used for further research; the Figure 4-10 illustrates the visual differences in biochars pyrolyzed at different temperatures.

250°C 350°C 550°C

Sawdust

Figure 4-10. The amount of pine sawdust in pyrolyzation (by furnace) and biochars (3 hr) at Highest Treatment Temperatures.

In addition to pine wood-waste, kanuka (*Kunzea ericoides*) sawdust was included for biochar preparation. Kanuka is a New Zealand native plant that is used for fuel and essential oils (Lis-Balchin et al., 2000). Some experiments included kanuka sawdust biochars manufactured at 350ºC for 3 hr and 12 hr (Figure 4-11). ***NOTE:*** *Column leaching results of the kanuka wood-waste and biochars are shown in Appendix A.*

Figure 4-11. Kanuka sawdust and biochar manufactured at 350ºC (3 hr).

In addition to the aforementioned biochars, a commercial pine 350ºC biochar (pyrolysis details unknown) was included subsequently referred to as "bulk biochar". This biochar was used in previous studies at Lincoln University (Gartler et al., 2013; Knowles et al., 2011; Robinson et al., 2011; Taghizadeh-Toosi et al., 2012b).

## 4.4 Characterization of biochars

### 4.4.1 Thermo-gravimetric analysis (TGA)

The TG analysis was conducted for the biochars, which were pyrolyzed using Kiln at 400, 550ºC, and the "bulk biochar". Samples were first homogenised (Figure 4-12), and a sub-sample was then finely ground for the TGA.

Figure 4-12. *Left to Right:* Sample homogenizer; sample grinder; TG analyzer.

Thermogravimetric analysis and the derivative (DTG) curves were obtained using TG analyzer SDT Q600, TA instrument, Melbourne, Australia (Pereira Calvelo et al., 2011). The samples (~ 20 mg) were placed in an alumina silica crucible (9-11 mm diameter) which is specific to the TGA. The crucible was then placed in the TG analyzer and heated from room temperature to 900$^{o}$C at a rate of 5$^{o}$C/min under a constant $N_2$ environment; once the target 900$^{o}$C was reached (holding time was 10 min), the $N_2$ supply was cut-off and air was introduced at a rate of 20 mL/min. Under the influence of air the sample burnt (holding time was 45 min) until it reached a constant weight where upon the sample was cooled to room temperature. The TG and DTG signals were exported to the TA Universal Analysis Software for data processing.

The percentage weight loss versus temperature was measured for each sample, and from the TG graph (Section 4.6.3 Biochar, Figure 4-13) the following parameters were measured:

(i) moisture content (as % - the weight loss at room temperature to 110$^{o}$C).

(ii) volatile matter content (% - the weight loss between 110-900$^{o}$C).

(iii) thermo resistant fraction or fixed C % (at 900$^{o}$C after the introduced the air flow until constant weight reached).

(iv) % ash (constant weight).

## 4.5 Wet chemical analysis

### 4.5.1 Bulk density

Bulk densities were determined using material which was oven-dried at 105°C. Bulk density was determined using Equation 4.1 (Topp & Dane, 2002).

$$\rho b = \frac{Ms}{Vt}$$ /Equation 4.1

Where,

$\rho_b$ = bulk density (g/cm$^3$)
$M_s$ = mass of oven dried materials (g)
$V_t$ = volume of the material (compacted in a measuring cylinder) (cm$^3$)

### 4.5.2 Moisture content

Moist soil cores and other materials were weighed and then oven-dried at 105°C, until a constant weight was reached. After cooling, these materials were reweighed, and the gravimetric moisture content (g $H_2O$/g dry material) was calculated as a percentage (Blakemore et al., 1987).

### 4.5.3 pH

The pH (in water) was measured using the method of Blakemore et al. (1987). Ten grams of material was mixed with 25 mL deionised water (DIW), stirred and left to stabilise overnight (24 hr). Then the pH was measured using a SevenEasy pH meter (Mettler Toledo, Columbus, OH, USA) which had been calibrated using buffers pH 4 and pH 7.

### 4.5.4 Extractable inorganic- N species ($NH_4^+$-N and $NO_3^-$-N) from the soil and biosolids

The extraction method was as described by Blakemore et al. (1987) and (Clough et al., 2001). Potassium chloride (KCl) 2M (AR grade) was used for the extraction. The extraction

solution was prepared by weighing 298 g of KCl and dissolving this in 2 L of deionised water. Four grams of sample material (field moist soil or fresh biosolids) were weighed into 50 mL plastic centrifuge tubes in duplicate and 40 mL of 2 M potassium chloride (KCl) (AR grade) added. Two blank samples were also included (solution only). The tubes were shaken for 1 hr on an end-over-end shaker. The samples were then centrifuged at 827 *g* for 10 min and filtered through Whatman™ 41 filter paper. Samples were analysed for $NH_4^+$-N and $NO_3^-$-N by the Flow Injection Analysis (FIA), Alpkem FS 3000 twin channel analyzer (Texas, USA) and inorganic N concentrations determined as follows:

$$Ns = \frac{(Ne \times V)}{Ms} \qquad \text{Equation 4.2}$$

Where;

Ns= Inorganic N content (mg/kg dry sample)

Ne= Inorganic N concentration of extract (mg/L)

V= Volume of solution (KCl + sample moisture) (L)

Ms= Mass of oven dry sample (kg)

## 4.5.5 Cation Exchange Capacity (CEC)

### 4.5.5.1 Reagents and Standards preparation

CEC and % of Base Saturation (BS) were measured using the method described by Blakemore et al. (1987). Silver thiourea (AgTU) 0.01 M reagent was prepared by dissolving 150 g thiourea in 3 L of de-ionized water in a 10 L container. Silver nitrate (16.99 g) was dissolved in 5 L of de-ionized water. The silver nitrate solution was then slowly added to the thiourea solution and made up to a final volume of 10 L.

Standards were prepared in five 100 mL volumetric flasks as below:

1. 100 mL thiourea,
2. 25 mL AgTU and 75 mL thiourea,
3. 50 mL AgTU and 50 mL thiourea,
4. 75 mL AgTU and 25 mL thiourea,

5. 100 mL AgTU

These standards corresponded to 0, $0.25\times10^{-2}$ M, $0.50\times10^{-2}$ M, $0.75\times10^{-2}$ M, and $1.0\times10^{-2}$ M AgTU.

#### 4.5.5.2 Extraction

Sample material was weighed (0.7 g) into 50 mL centrifuge tubes, 35 mL of 0.01 M AgTU was added and the samples were shaken on an end-over-end shaker for 16 hr. Samples were then centrifuged at 827 *g* for 10 min and filtered through Whatman™ 40 filter paper and collected in plastic vials. These samples were analysed for Ag, Mg, Ca, K and Na on an Inductively Coupled Plasma Optical Emission Spectrometer ICP-OES (Varian 720 –ES, Australia), fitted with an SPS-3 auto-sampler and ultrasonic nebulizer.

#### 4.5.5.3 Calculation for CEC

$$CEC = (1 - N) \times 50 \qquad \text{Equation 4.3}$$

Where;
CEC: Cation Exchange Capacity ($cmol_c/kg$)
N: Ag concentration (μg/mL)

##### *4.5.5.3.1 Calculations for % of Base Saturation (% BS)*

The concentrations of Mg, Ca, K and Na were used to calculate % BS. The following appropriate equations were used to calculate the ions Mg, Ca, K and Na, the concentrations given in $cmol_c/kg$.

$$Mg = \frac{(\mu g / mL - blank) \times 0.29}{Wt} \qquad \text{Equation 4.4}$$

$$Ca = \frac{(\mu g / mL - blank) \times 0.175}{Wt} \qquad \text{Equation 4.5}$$

$$K = \frac{(\mu g / mL - blank) \times 0.09}{Wt}$$ Equation 4.6

$$Na = \frac{(\mu g / mL - blank) \times 0.15}{Wt}$$ Equation 4.7

Where;
µg/mL = Appropriate ion concentration in the extract
blank= Appropriate ion concentration in the blank AgTU
Numerical factor = Unit conversion factor for a specific ion

$$\%\, Base\ \ Saturation = \frac{\sum(Ca + Mg + K + Na) \times 100}{CEC\,(cmolc / kg)}$$ Equation 4.8

## 4.5.6 Total elemental analysis

### 4.5.6.1 Pasture

#### *4.5.6.1.1 Sample preparation*

Total elemental analyses of the pasture samples (dried and finely ground <2 mm) were performed using microwave digestion (Microwave Solvent Extraction Labstation (Ethos SEL), Italy). In digestion tubes, 8 mL of Aristar™ nitric acid (±69%) was added to 0.5 g of sample. Samples were pre-digested overnight. Samples were placed on the microwave rotor and the temperature ramped up to 170ºC over 20 min, with a holding period of 20 min. The digests were then cooled to room temperature and filtered using Whatman 52 filter paper and made up to 25 mL with milliQ water (double de-ionised water) and stored in a refrigerator at 4ºC (the analyses occurred within 3 days).

#### 4.5.6.2 Soil, sawdust, biochars, lignites and biosolids digests

##### *4.5.6.2.1 Sample preparation*

Total elemental analyses of these materials (dried and finely ground <2 mm) were performed using microwave digestion (Microwave Solvent Extraction Labstation (Ethos SEL), Italy). In digestion tubes, 5 mL of conc. $HNO_3$ and 1 mL of $H_2O_2$ (Merck hydrogen peroxide 30%) were added to 0.5 g of sample, mixed well and pre-digested overnight. Samples were placed on the microwave rotor and the temperature was ramped up to 175$^{o}$C over 10 min, with a holding period of 20 min. Samples were allowed to cool to room temperature, then filtered using Whatman 52 filter paper into 25 mL volumetric flasks with milliQ water and stored in a refrigerator.

#### 4.5.6.3 Analysis

Concentrations of general metals such as Al, As, B, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, and Zn were determined using ICP-OES (described in CEC methods). Reference soil and plant materials (International Soil analytical Exchange — ISE 921 and International Plant analytical Exchange IPE 100) from Wageningen University, Netherlands, were analysed for quality assurance. Recoverable concentrations were between 91% – 108% of the certified values.

### 4.5.7 Total N and C

Total C and N concentrations were analysed using an Elementar Vario-Max CN Elemental Analyzer (Elementar GmbH, Hanau, Germany). The samples were combusted at 900°C in an oxygen atmosphere. The combustion process converted any elemental C and N into $CO_2$, $N_2$ and $NO_x$. The $NO_x$ was subsequently reduced to $N_2$. These gases were then passed through a thermal conductivity cell to determine $CO_2$ and $N_2$ concentrations and the % C and % N were calculated from the initial sample weights combusted.

### 4.5.8 Water Soluble Carbon (WSC)

WSC was determined in two steps, cold water soluble C and hot water soluble C, using the method described by Ghani et al. (2003).

#### 4.5.8.1 Cold water extract

Three grams of oven-dried material and 30 mL of cold distilled water were placed in polypropylene centrifuge tubes on an end-over-end shaker for 30 min and then centrifuged for 20 min at 2253 *g*. The extracts were then decanted off and filtered through 0.45 μm cellulose nitrate membrane filters and stored in a refrigerator prior to analysis.

#### 4.5.8.2 Hot water extract

A further 30 mL of distilled water was added to the sample remaining in the centrifuge tube which was then placed in a hot water bath at 80ºC for 16 hr centrifuged for 20 min at 2253 *g* and then filtered through 0.45 μm cellulose nitrate membrane filters. Total Carbon (TC), Inorganic Carbon (IC) and Total Organic Carbon (TOC) concentrations of the WSC samples were measured using a TOC-5000A analyzer (Shimadzu Oceania Pty Ltd, NSW, Australia) fitted with a Shimadzu ASI-5000A autosampler. Equation 4.9 was used to calculate the WSC in both sets of extracts.

$$WSC = \frac{(TOC \times V)}{Md}$$ Equation 4.9

Where;
WSC= Water soluble carbon (mg/kg)
TOC = Total organic carbon concentration of extract (mg/L)
V = volume of solution (L)
Md = Mass of oven dry material (kg)

### 4.5.9 Statistical analysis

Statistical analysis of data was performed using Minitab® version 16 (Minitab Inc., State College, Pennsylvania, USA). One-way analysis of variance (ANOVA) was used to determine if treatment means differed, and when differences occurred the comparison between means was made using Fisher's individual error rate with least-significant-difference method ($p$ <0.05). Data were tested for normality before performing ANOVAs, with 95% confidence limits ($p < 0.05$) used to indicate levels of significance.

## 4.6 Results and Discussion

### 4.6.1 Biosolids

Table 4.1. Physical and chemical properties of biowaste at different stages of treatment (from literature), including the Kaikōura biosolids (KBS) used in this research.

| | Kaikōura biosolids (KBS) | Raw sludge | Aerobic sludge | Anaerobic sludge | Digested dry sludge | [a]Aged biosolids |
|---|---|---|---|---|---|---|
| **General analysis** | | | | | | |
| pH | 4.5 | 5.5-6.5 | 7.6 - 8.2 | 5.8 -8.1 | 6.4 -7.3 | 4.4 - 4.5 |
| EC (dS/m) | n/a | 0.4 | 2.2 (1.7) | 4 | 5.5 (0.4) | 2.4 (0.8) |
| Organic matter % | n/a | n/a | 74 (8.5) | 14 | 53 (9.5) | n/a |
| CEC ($cmol_c/kg$) | 16.7 (0.7) | 53.5 | 101 | n/a | 39 | n/a |
| Base saturation (%) | 107 (2.3) | n/a | n/a | n/a | n/a | n/a |
| Dry solids % | 51 (2.2) | 6.2 (0.3) | 2.3 | 1.7 (0.2) | 94 | 65 |
| Volatile solids % | n/a | 85 | n/a | n/a | n/a | 26 |
| $NH_4^+$ (mg/kg) | 130 (7.3) | n/a | 208 | 520 | 4732 | 208 |
| $NO_3^-$ (mg/kg) | 1352 (2.5) | n/a | 526 | 100 | 431 | 1848 |
| **Organic elemental analysis** | | | | | | |
| Total C % | 30 (0.5) | 44 (0.05) | 41 (1.8) | 41 (4.5) | 38 (1) | 23 |
| Total N % | 3.1 (0.06) | 2.2 (0.1) | 4.8 (2) | 9.3 (4.2) | 4.7 (0.9) | 1.9 |
| Organic N % | n/a | 2 | 3.6 | n/a | 4.1 | n/a |
| C/N | 9.7 (0.02) | 20 (1.1) | 8.5 (2.7) | 4.4 | 8.1 (1.3) | 12.1 |
| **Inorganic elemental analysis (mg/kg)** | | | | | | |
| Al | 17351 (500) | 3242 (962) | 6522 | 11412 | 8618 | 21709 (333) |
| As | n/a | 2.2 (1.8) | 6.8 (3.2) | 16 | 0.5 | 22 (3.5) |
| Cd | 2.3 (0.1) | 0.9 (0.3) | 2 (0.8) | 3.7 (1.8) | 3 (2.3) | 20 (4) |
| Ca | 9455 (534) | 15450 (8450) | 21348 | 48294 | 4268 | 11953 (441) |
| Cu | 637 (39) | 138 (9.5) | 161 (113) | 437 (106) | 300 (105) | 689 (105) |
| Cr | 34.2 (0.3) | 239 (206) | 408 (396) | 1022 (208) | 114 | 776 (208) |
| Fe | 8352 (221) | 2794 (274) | 4253 (2573) | 9882 | 28450 (14550) | 16925 (2962) |
| Pb | 114 (5.5) | 60 (0.0) | 73 (42) | 240 (15) | 140 (60) | 497 (112) |
| Mg | 2994 (55) | 1995 (46) | - | 15833 | 3495 (455) | 1746 (46) |
| Mn | 189 (2.2) | 75 929) | 159 (66) | 369 | 196 (1) | 103 (17) |
| Hg | n/a | 0.6 (0.3) | 0.8 | 2.8 | 0.4 | 6.8 (0.8) |
| Ni | 26.4 (1) | 19.5 (11) | 61 | 91 | 17.3 (1.8) | 155 (29) |
| P | 3463 (248) | 3100 | 1400 | 3710 (3290) | 15444 (5729) | 5737 (120) |
| K | 3014 (173) | 2814 (696) | 4565 | 18206 | 2887 (1152) | 3171 (78) |
| Se | n/a | 1 (0.2) | 3 | 5.3 | 2 | n/a |
| Na | 299 (12) | 4959 (719) | 3957 | 6647 (353) | 2170 (1919) | 1744 (59) |
| S | 6736 (250) | n/a | n/a | 40000 | n/a | 12771 (4079) |
| Zn | 1047 (69) | 325 (86) | 617 (280) | 1647 (47) | 859 (323) | 1611 (373) |

1)[a]Aged biosolids was a combined study of Nash et al. (2011), Laidlaw et al. (2012) and Mok et al. (2013) (2) values are an average with standard error (stderr) in parenthesis (n $2 \leq 5$ ). The values with no stderr are from a single publication (3) Electrical Conductivity (EC).

The pH of the KBS was acidic in nature (pH 4.5) as was that of the aged biosolids, while the pH of the biowastes, at different treatment stages, ranged between pH 5.8 and 8.2.

The CEC value was also lower (16.7 $cmol_c/kg$) in the KBS compared to composted sludge and aerobic sludge (125 and 101 $cmol_c/kg$ respectively). The CEC value of KBS was closer to that of digested dry sludge/biosolids (39 $cmol_c/kg$), unfortunately CEC values of the aged biosolids were not reported by the authors (Nash et al., 2011).

According to Bernal et al. (1998) matured biosolids have higher $NO_3^-$ and lower $NH_4^+$ concentrations than fresh biosolids. This was observed in the KBS, with 1352 mg/kg of $NO_3^-$ and 130 mg/kg of $NH_4^+$). Kaikōura District Council's records showed that the KBS were collected from a 20-30 yr old stockpile. In Melbourne, Australia, the Western Treatment Plant (WestTP) was established in the 1890's. Annually it produces 20,000 t of biosolids and roughly a million tons are stockpiled (Laidlaw et al., 2012). The aged biosolids properties reported by Nash et al. (2011), Laidlaw et al. (2012) and Mok et al. (2013) were from biosolids collected from WestTP, Melbourne (Table 4.1). In comparison, all of the sludges at a different level of digest showed much lower amounts of $NO_3^-$and greater amounts of $NH_4^+$, indicating these were reasonably new sewage sludges. The higher $NO_3^-$ levels of the KBS indicates there would be a tendency for $NO_3^-$ to leach when used as a soil amendment. As nitrate is negatively charged, it would not be bound via CEC on the carbonaceous materials.

Total % C of the six biosolids types in Table 4.1 ranged between 23-44%, with the KBS at 30%. Total % N was between 1.9-9.3%, with KBS at 3.1%. Anaerobic sludge had the highest value at 9.3%. Total C values should approximate to the organic C value [organic C = total C-inorganic C (Pereira Calvelo et al., 2011)], because inorganic C contents were negligible as dissolved inorganic carbon (DIC) [carbonate is a function of pH (at pH 8.2 there is potential for DIC to be present, but it may be negligible compared to the organic C pool) degradation in the C pool can be caused by exposure to heat and sunlight (UV) and also microbial degradation can take place in biosolids stockpiled more than 20 years]. However, the C/N ratio was slightly lower in KBS (9.7) than the aged biosolids (12.1), while raw sewage had the highest C/N value

(20) as expected. In KBS, trace elemental components showed elevated values for some elements e.g. Al, Cu and Zn, while aged biosolids generally had high concentrations of most ions (Table 4.1).

According to Wayne et al. (2015), the total C content can be used to estimate Organic Matter OM) by multiplying it by 1.72 (organic matter= total organic C% × 1.72). Using this equation, the KBS's OM content was equal to 51.6%. This is lower than the raw sewage and other digested sludge. Melbourne's WestTP aged biosolids contained the lowest amount of OM (~21%). Organic matter degrades with aging (Samaras et al., 2008). Higher values for OM, N, P, S were usually observed in freshly digested biosolids, however, lower nutrient concentrations were given for settlement pond biosolids, composted biosolids, and alkaline-stabilized biosolids (Sullivan et al., 1998). Therefore, it was expected that most of the existing OM in the KBS was more resistant to degradation than the OM from fresh biosolids, because most of the degradable OM in KBS may have already been broken down due to the age of the stockpile. Thus, if KBS were applied to land as a fertilizer there is the potential for excess $NO_3^-$ to leach.

When biosolids are stockpiled over the long term, ground water can become polluted (Peckenham et al., 2008) and Green House Gases (GHG) are emitted (Majumder et al., 2014). Therefore, leaving stockpiled biosolids for the long term will contaminate the soil, air and ground water. These piles should be removed at regular intervals to protect the environment. This may be possible if this research proves that biosolids application is suitable to rebuild degraded soil with minimal $NO_3^-$ released to the environment.

### 4.6.2 Sawdust

Pine sawdust contained 510 g/kg total C, close to that found in typical sawdust [(Wilen, et al. 2004) Table 4.2], while total N was 0.6 g/kg, lower than the 4g/kg of typical sawdust. The total C and N of the typical pine feedstock was given by Pereira Calvelo et al. (2011) as 487 and 2 (g/kg), respectively. Other studies show pine feedstock values for ash, volatiles and fixed C were 1.8%, 89.8% and 8.3%, respectively (Enders et al., 2012).

Table 4.2. Physical chemical properties of pine sawdust (feedstock for biochars in this research).

| | **Pine sawdust (current study)** | **Typical sawdust** |
|---|---|---|
| **General analysis** | | |
| pH | 5.7 | 7.6 |
| CEC ($cmol_c/kg$) | 10.6 | n/g |
| Bulk density ($g/cm^3$) | 0.2 | n/g |
| Base saturation (%) | 448 (6.8) | n/g |
| WSC-C (mg/kg) | 6063 (21) | n/g |
| WSC-H (mg/kg) | 5150 (14) | n/g |
| Ash (%) | n/a | 1.4 (0.5) |
| Volatile matter (%) | n/d | 72.4 (4) |
| **Organic elemental analysis** | | |
| Total C % | 51. (0.04) | 51.8 (0.3) |
| Total N % | 0.06 (0.001) | 0.4 (0.01) |
| C/N | 850 | 128 (0.2) |
| **Inorganic elemental analysis (mg/kg)** | | |
| Al | 0.6 (0.2) | n/g |
| As | <0.001 | <1 |
| Cd | <0.001 | <0.05 |
| Ca | 1059 (29) | n/g |
| Cr | 0.9 (0.06) | <4 |
| Fe | 23.2 (6) | 66 |
| Pb | <0.005 | <1 |
| Mg | 443 (2.9) | n/g |
| Mn | 86 (0.9) | 102 |
| P | 50 (0.06) | n/g |
| K | 921 (6.8) | 480 |
| Na | 963 (67) | 20 |
| S | 87 (0.1) | n/g |
| Zn | 9.3 (0.08) | 8.9 |

n/g- the values were not given, n/d- not determine, n/a- not analysed. Typical sawdust inorganic analysis data were analysed from the ash (Wilén et al., 2004).

The sawdust used in this research showed only trace levels of the hazardous elements Cd, Cr and As.

Basic analysis of pH, total N and C were conducted for kanuka sawdust (Table 4.3). Total C was 498 g/kg, similar to that of pine, while total N was at 0.8 g/kg. A single column leaching experiment was conducted with kanuka wood-waste (because it was included in this study at a later stage).

Table 4.3. Basic properties of Kanuka wood-waste and biochars.

| | pH | N (%) | C (%) | C/N |
|---|---|---|---|---|
| Kanuka wood-waste | 4.9 | 0.08 (0.006) | 49.8 (0.03) | 576 (31) |

Kanuka wood-waste is not readily available around the country and permission to harvest it is required from the Department of Conservation (DOC), as well as purchase of the wood. It does not fulfil the requirements as an amendment material of low cost, and is not easily obtained in sufficient quantities.

### 4.6.3 Biochar

Pereira Calvelo et al. (2011) characterised pine, poplar and willow wood-waste biochars to estimate the labile fraction of C. The same centre facilities were used for a part of this current study, mainly biochar pyrolyzation. Characterizations of these biochars from the TGA are shown in Table 4.4 and general properties are shown in Table 4.5 and Figure 4.13.

Table 4.5

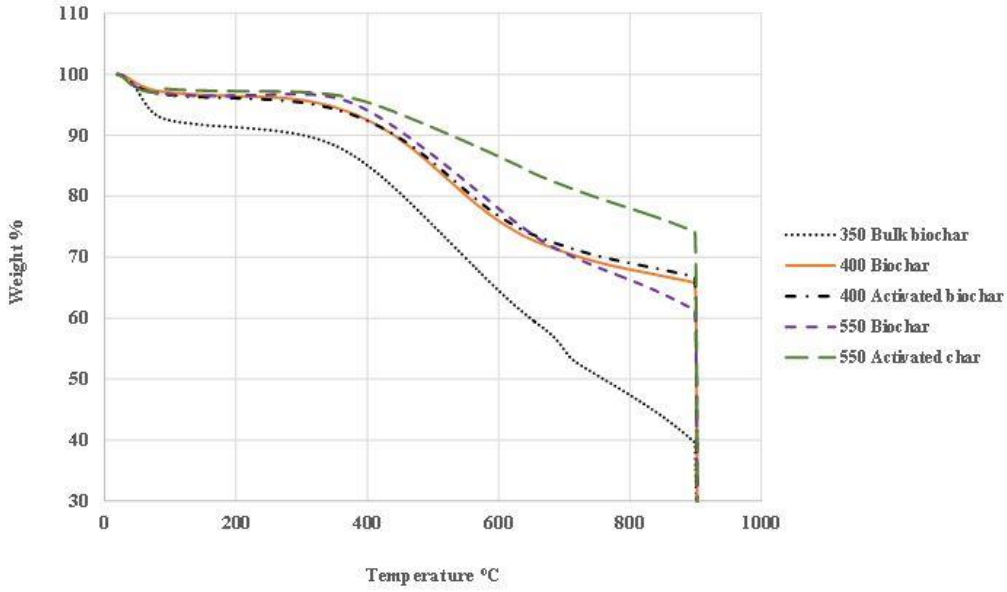


Figure 4-13. TGA graph for five types of biochars with and without steam activation. Numerals indicate maximum pyrolysis temperature.

As expected, the commercially prepared "bulk biochar" had more unpyrolyzed material than biochars prepared at 400ºC and 550ºC. Increasing pyrolysis temperature decreased the volatile C content and increased values for fixed C (Figure 4.13). A similar pattern was shown by Pereira Calvelo et al. (2011) with woody (pine, poplar) biochars and also by Brewer et al. (2011), where they used corn stover and switchgrass (at 550ºC). The activated biochars showed slightly less volatile/labile C (Singh et al., 2012) compared to the non-activated biochars, and retained more. Ash content did not vary significantly for the biochars used in this current study (Table 4.4). Ash content was lower where biochars were produced with woody material compared to corn stover or switchgrass (Table 4.6).

Table 4.4. Measurements from the TGA graph Figure 4-13.

| | Moisture (%) | Volatile matter (%) | Fixed carbon (%) | Ash (%) |
|---|---|---|---|---|
| 350°C "Bulk biochar" | 7.9 | 53 | 36.2 | 3.3 |
| 400°C "A" Biochar | 2.5 | 30 | 64.3 | 3.4 |
| 400°C Biochar | 2.5 | 32 | 62.4 | 3.3 |
| 550°C "A" Biochar | 2.4 | 23.2 | 71 | 3.4 |
| 550°C Biochar | 2.4 | 35.7 | 58.6 | 3.4 |

Note: "A" is steam activated biochar.

The pH values of the biochars pyrolyzed for this research ranged between 5.5 to 8.1 (Table 4.5). Lower temperature biochars had lower pH values, this trend was also shown by Lehmann (2007), where pH gradually increased from 4 -12 over a 200 – 800°C pyrolysis range. An exception to this was the 'bulk biochar" (as mentioned before this was a commercially pyrolyzed biochar) in this study which had higher pH than 400°C char. Activated biochars showed a slight increase in pH. Zhang et al. (2015) also showed a similar pH trend of 4.9, 6.9 and 9.5 as pyrolysis temperature increased from 200°C, 400°C and 600°C, respectively (Table 4.6).

Table 4.5. Basic chemical properties of biochars used in this study.

| | pH ($H_2O$) | CEC ($cmol_c/kg$) | Base saturation (BS) % | C % | N % | C/N | WSC-C | WSC-H |
|---|---|---|---|---|---|---|---|---|
| Biochar 350°C, 3 hr | 5.5 | 2.2 | 111 | 71 (0.09) | 0.03 (0.002) | 2761 (184) | 462 (20) | 1043 (57) |
| Biochar 350°C, 12 hr | 5.5 | 1.3 | 265 | 72.8 (0.1) | 0.03 (0.007) | 2380 (454) | 375 (6.2) | 431 (16) |
| Bulk biochar 350°C | 6.9 | 9.1 | 88 (2.2) | 78 (0.08) | 0.06 (0.02) | 1797 (37) | 1468 (28) | 3054 (137) |
| Biochar 400°C A | 6.2 | 5.9 | 50 (0.3) | 75.5 (0.07) | 0.04 (0.004) | 1793 (157) | 1182 (89) | 1876 (34) |
| Biochar 400°C | 5.9 | 5.2 | 52 (5.0) | 75.3 (0.07) | 0.04 (0.01) | 1932 (37) | 1300 (20) | 2054 (72) |
| Biochar 550°C A | 8.1 | 6.7 | 94 (2.4) | 88.4 (0.1) | 0.03 (0.01) | 2666 (548) | 833 (75) | 407 (7) |
| Biochar 550°C | 7.9 | 6.7 | 58 (6.2) | 86.5 (0.06) | 0.03 (0.002) | 2446 (641) | 150 (7) | 339 (9) |
| Kanuka char 350 (3hr) | 6.1 | n/a | n/a | 73.3 (0.05) | 0.06 (0.02) | 1701 (247) | n/a | n/a |
| Kanuka char 350 (12hr) | 5.3 | n/a | n/a | 74.2 (0.07) | 0.04 (0.002) | 1974 (85) | n/a | n/a |

WSC-C and –H: water soluble carbon cold and hot extract (see Methods for detail).
*NOTE:* It is very important to measure the molar $H/C_{org}$ to characterize a biochar, according to the International biochar initiative (IBI), where they mentioned that the value provides crucial information of what degree of aromatic C at the end of that pyrolyzation. In this current study I did not measure the H/C ratio, because I was interested in low-tech biochars.

Table 4.6. Typical biochar characteristics (Enders et al., 2012; Hina et al., 2010; Pereira Calvelo et al., 2011; Zhang et al., 2015).

| Feedstock | HTTs | pH ($H_2O$) | C% | N% | H% | O% | CEC $cmol_c/kg$ | BS% | Ash% | Volatiles% | Fixed C % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Pine | 350 | 5.1 | 71 | 0.1 | 5 | 25 | 29 | 22 | 1.2 (0.6) | 45 (12) | 55 (12) |
| | 400 | 6.9 | 77 | 0.6 | 4.6 | 14.5 | 30 | 0.1 > | 2.3 (0.8) | 38.2 (4.5) | 59.6 (4.1) |
| | 550 | 6.1 - 10 | 83 (2.8) | 0.4 (0.2) | 3.3 (0.1) | 12 (2.8) | 25 | 12 | 3.4 (0.9) | 27 (6.5) | 69 (5.2) |
| Corn Stover | 500 | 6.5- 9.9 | 54 (10) | 1.1 (0.2) | 3 (0.3) | 10 (2.5) | 40 (12) | 142 | 33 (8) | 29 (2.4) | 38 (13) |
| | 550 | 6.6 – 10 | 55 (18) | 0.9 (0.3) | 2.8 (0.5) | 13 (1) | 28 | n/a | 29 (15) | 34 (3.7) | 37 (12) |
| | 600 | 6.7 -10 | 51 (20) | 0.9 (0.3) | 2.2 (0.2) | 9.3 (0.05) | 33 (6.5) | 172 | 36 (20) | 21 (3.5) | 43 (17) |
| Switchgrass | 450 | 6.2 | 38 | 0.5 | 2.2 | 9 | 28 | n/a | 50 | 17 | 32 |
| | 500 | 6.6 | 52 (12) | 1.2 (0.7) | 2 | 2.4 | 26 | n/a | 55 | 32.3 (21) | 36 (4.3) |
| | 550 | 6.7 | 42 | 0.5 | 2 | 5 | 26 | n/a | 50 | 14 | 35 |
| Popular | 400 | 7.2 -9 | 55 (17) | 0.6 (0.2) | 3.4 (1.1) | 38 (19) | n/a | n/a | 2.9 (0.9) | 35 | 61 |
| | 550 | 8.8 | 76 | 1 | 3.6 | 13 | n/a | n/a | 6.5 | 28 | 66 |
| Oak | 400 | 4.6-6.9 | 64 (11) | 0.4 (0.2) | 3.2 | 17.1 | 51.3 (9.9) | 15 | 0.8 | 37 (4.5) | 58 |
| | 600 | 6.4-9.5 | 72 (13) | 0.4 (0.09) | 2.5 | 8.5 | 54.8 (42) | 7.5 | 1.3 | 20.2 (7.9) | 71 |
| Oak (with Steam activation) | 400 | 9.6 | 30.3 | 0.5 | n/a | n/a | 36.2 | n/a | n/a | n/a | n/a |
| | 600 | 9.6 | 37.1 | 0.4 | n/a | n/a | 42.6 | n/a | n/a | n/a | n/a |

n/a: values not given by the authors; the value along with brackets gives an average of that parameter from a similar kind of biochar (same feedstock & Highest Treatment Temperatures (HTT) taken in to account) done by different authors (minimum 2 or maximum up to 4); values without the brackets are from a single study.

The CEC values of the biochars used in this study were 1.3 to 6.7 $cmol_c/kg$ except the "bulk biochar" which had the highest CEC (9.1 $cmol_c/kg$). These biochars had lower CEC values when compared to the pine biochars made at 350, 400 and 550$^oC$, reported on by Enders et al. (2012) which ranged from 25 -30 $cmol_c/kg$. Other biochars (Table 4.6) were shown to have CEC values > 25 $cmol_c/kg$, but with no relationship with feedstock or pyrolysis temperature.

Base saturation (BS) values were lower as pyrolysis temperature declined with a large variation in the range of 50 -265%. However, Enders et al. (2012) found a BS of between 7.5 - 15% for woody (oak and pine) biochars and found higher values (142-172%) for corn stover. This observation related to the ash content of that particular biochar.

In the current study, total C% value generally increased from 71 - 89 % with increasing pyrolysis temperature The C values for biochars used in this research were similar to that of other studies (Table 4.6), but N values were at least 10-fold lower (0.04%), ranging from 0.1 - 1.1%.

Biochars' macro elements and important micronutrient analysis results from this research are given in Table 4.7 and Appendix A. There have been few previous studies examining the nutrient content of biochars. Kloss et al. (2012) used water to extract elements from biochars, and these values are given in Appendix A and another study by Enders *et al*., (2012) which analysed elements from an acid digest of some biochars (Appendix A).

Table 4.7. Macro elements (acid digestion) in the pine wood-waste and biochars from the current study, values are in mg/kg,

| | **Na** | **K** | **Ca** | **Mg** | **S** | **P** |
|---|---|---|---|---|---|---|
| Biochar 350°C, 3 hr | 762 (20.8) | 1400 (48.7) | 1667 (92) | 511 (23.4) | 107 (3.4) | 79.3 (4) |
| Biochar 350°C, 12 hr | 1620 (17.6) | 2211 (7.8) | 3012 (31.9) | 889.2 (1.8) | 160.9 (1.5) | 148.1 (1.5) |
| "Bulk biochar" 350°C | 2504 (15) | 4795 (16.6) | 37767 (66) | 2038 (13.5) | 1268 (11.3) | 834 (8.0) |
| Biochar 400°C A | 2062 (35) | 4782 (24.7) | 5530 (23) | 1723 (21) | 413 (0.8) | 627 (4.9) |
| Biochar 400°C | 1845 (53.5) | 4443 (92.0) | 5343 (156) | 1696 (27.6) | 392 (4.4) | 587 (12.6) |
| Biochar 550°C A | 1965 (19.3) | 4474 (16.1) | 5097 (15.8) | 1756(4) | 272.8 (1.0) | 596 (0.6) |
| Biochar 550°C | 2032 (33) | 4863 (28) | 5453 (35) | 1752 (2.2) | 628 (120) | 730 (18.2) |

Table 4.8. Micro elements (acid-digestion) in pine wood-waste and biochars of the current study, values are in mg/kg.

| Pyrolysis | Al | As | Cd | Cr | Fe | Mn | Pb | Zn |
|---|---|---|---|---|---|---|---|---|
| Biochar 350°C, 3 hr | 0.6 (0.06) | 0.06 (0.007) | 0.002 (0.0002) | 1.5 (0.1) | 7.1 (0.4) | 2.9 (0.1) | n/d | 0.4 (0.06) |
| Biochar 350°C, 12 hr | 1.0 (0.002) | 0.04 (0.003) | 0.003 (0.0002) | 3.9 (0.13) | 6.3 (0.6) | 4.9 (0.003) | n/d | 0.8 (0.01) |
| "Bulk biochar" 350°C | 8.5 (0.2) | 0.09 (0.002) | 0.02 (0.0001) | 0.02 (0.003) | 74.4 (0.4) | 29.6 (0.2) | 0.07 (0.006) | 1.5 (0.03) |
| Biochar 400°C A | 5.06 (0.1) | 0.03 (0.002) | 0.01 (0.0001) | 0.05 (0.007) | 6.9 (0.03) | 11.8 (0.2) | 0.03 (0.002) | 1.6 (0.008) |
| Biochar 400°C | 6.3 (0.2) | 0.03 (0.007) | 0.01 (0.0002) | 0.06 (0.005) | 9.5 (0.2) | 11.1 (0.3) | 0.03 (0.0005) | 1.4 (0.04) |
| Biochar 550°C A | 6.7 (0.04) | n/d | n/d | 0.07 (0.001) | 6.5 (0.08) | 11.3 (0.007) | 0.02 (0.003) | 1.2 (0.003) |
| Biochar 550°C | 6.4 | n/d | n/d | 0.09 | 6.5 | 11.8 | 0.06 | 1.3 |

n/d –not detected: A- Activated biochar. The values are significantly lower than the minimum allowed by International Biochar Initiative (IBI) standards.

### 4.6.4 Lignite

Lignite is a heterogeneous compound, its character (chemical and physical) is mainly influenced by the geography of where the mine is located (details are given in Chapter 3) and the surrounding environment. The New Vale (NV) lignite, Charleston (CH) lignite and Millerton (M) lignite (Table 4.9) were compared with the properties of a standard lignite (IHSS) and a combined lignite (average of five European lignite).

Table 4.9. Physical and chemical properties of the lignites used in this research and standard lignite (Janos et al., 2011).

| | New Vale | Charleston | Millerton | [a]Standard lignite | Combined lignite |
|---|---|---|---|---|---|
| pH ($H_2O$) | 4.5 | 4.1 | 3.4 | 4.2 | 5.1-6.2 |
| Moisture % | 38 (0.36) | 47.9 (0.38) | 1.2 (0.002) | 12.3 | 11.7 (0.4) |
| Ash % | n/a | n/a | n/a | 14 | 19 (1.2) |
| CEC ($cmol_c/kg$) | 43.6 (0.8) | 14.7 (0.2) | 2.1 (0.3) | n/g | n/g |
| Base saturation (%) | 115.3 (0.5) | 125.2 (2.5) | 15.3 (4) | n/g | n/g |
| Bulk density (g/cm3) | 0.6 | 0.8 | 0.7 | n/g | n/g |
| WSC-cold (mg/kg) | 901(30) | 203 (8) | 3.4 (3) | n/g | n/g |
| WSC-hot (mg/kg) | 3028 (63) | 1026 (4) | 77 (4) | n/g | n/g |
| **Organic elemental analysis** | | | | | |
| Total C (%) | 86 (0.4) | 56 (1.4) | 52 (0.6) | 65 | 63.4 (0.2) |
| Total N (%) | 1.3 (0.01) | 0.9 (0.04) | 0.9 (0.02) | 1.2 | 0.9 (0.04) |
| C/N | 69.8 (0.3) | 64.5 (1.8) | 56.3 (0.4) | 54.2 | 69.3 (2.8) |
| **Inorganic elemental analysis (mg/kg)** | | | | | |
| Al | 2488 | 3629 (48.9) | 134 (1.3) | 8000 | 16600 (0.2) |
| B | 36.3 (0.1) | 211.2 (24) | 23.4 (0.6) | n/d | n/d |
| Cd | 0.06 | 0.1 (0.0) | 0.04 (0.0) | n/d | n/d |
| Ca | 17502 | 1850 (190) | 51.9 (1.1) | 13000 | 17000 (0.05) |
| Cu | 2 (0.0) | 3.85 (0.4) | 1.9 (0.0) | n/d | n/d |
| Cr | 2.4 (0.0) | 9.2 (0.5) | 0.3 (0.0) | n/d | 100 |
| Fe | 12918 (145) | 3490 (198) | 1704 (184) | 5000 | 9800 (0.2) |
| Mg | 2815 (11) | 779.4 (85) | 13.4 (0.8) | 3000 | 3200 (0.08) |
| Mn | 280 (3) | 30.3 (2) | 1.45 (0.1) | 100 | 167 (0.005) |
| Ni | 4.4 (0.1) | 6.3 (0.5) | 1.2 (0.04) | n/d | 100 |
| P | 57.6 (0.2) | 478.3 (50) | 4.2 (0.3) | n/g | n/g |
| K | 219 (2) | 295 (21) | 30.8 (1.6) | n/g | n/g |
| Na | 176 (1.1) | 94 (3.7) | 69 (1.5) | n/g | n/g |
| S | 6539 (35) | 6180 (589) | 13799 (455) | 7000 | 17400 (0.16) |
| Zn | 9 (1) | 20 (2.2) | 35.5 (1.2) | n/d | 300 |

[a] standard lignite (issued by IHSS) and "combined lignite" is given as an average of 5 lignite from different parts of central Europe; WSC- Water Soluble Carbon; n/d – not detected; n/g- not given; n/a – not analysed.

Janos et al. (2011) characterised lignite from central European mines using a standard lignite issued by the International Humic Substances Society (IHSS), as a reference material and this is denoted as the "Standard lignite" in Table 4.9.

The moisture contents of New Vale and Charleston lignites were significantly higher than other lignites, at 38 and 48%, respectively, compared to the Millerton lignite at 1.2%, the Standard lignite at 12.3% and the combined lignite at 11.7%. Comparison of pH values showed that Millerton lignite was the most acidic at 3.4, while Charleston, Standard and New Vale lignites were similar (at 4.1, 4.2 and 4.5 respectively). The combined lignite pH varied between 5.1-6.2 pH. Total C varied between 52% for the Millerton lignite to 86% for the New Vale lignite, while total N was similar between lignites, ranging from 0.9 – 1.3%. Metallic elements showed considerable variation in the presence and amount of certain elements. Co was not detected in the Standard or combined lignites while it was present in all three New Zealand lignite. Cr was not detected in the Standard lignite, but it was found in trace amounts in the three New Zealand lignites, and was high (100 mg/kg) in the combined lignite. The Al content of the three New Zealand lignites was significantly ($p<0.05$) lower than those of the Standard and combined lignites, with Millerton exceptionally low at 134 mg/kg. The concentration of Mn was highest in the New Vale lignite (280 mg/kg) (Table 4.9), and also higher than the Standard and combined lignites. The highest CEC value, of 43.6 $cmol_c/kg$, was found in the New Vale lignite. Thus greater $NH_4^+$ retention should occur in the New Vale lignite. All three lignites had high C/N ratios and this feature could be the key for immobilization of N (Chapters 2 and 3).

## 4.7 Conclusions

Following biochar characterization, the pine sawdust, biochars pyrolyzed at 350, 400 and 550$^{o}$C and the New Vale lignite were selected for further experiments. Kanuka wood-waste is not readily available and is thus not commonly used as a wood-waste as timber or heating source (fuel). However, it was included at a later stage because of its anti-microbial properties (Wyatt et al., 2005). On the other hand, pine sawdust is readily available throughout the year around New Zealand and most of the time it is free.

The low CEC values of biochars that were pyrolyzed at 350$^{o}$C, 400$^{o}$C and 550$^{o}$C were unexpected, as other authors found biochars to have high CEC values. Any significant sorption observed by any of the low CEC chars, is likely to be dominated by physical sorption processes, not chemical.

Lignite characterization showed a wider variation in measured parameters than the biochars. Generally lignite related research is performed with a focus on lignite as a fuel/energy source and there are few studies that report values for CEC, base saturation or WSC (except: Simmler et al. (2013).

The biosolids used in this research were from a small town, Kaikōura, on the east coast of the South Island of New Zealand. However, the biosolids in Kaikōura have similar properties to the “aged biosolids” from the Melbourne WestTP (details of the WestTP production were given at the beginning of this discussion). Another common character of these two biosolids was their acidic (without the lime stabilization) nature. However, biosolids widely used in scientific research have a pH range between 6-10. These biosolids were mostly treated for microbes (by raising the pH), therefore these biosolids can be used for land application and other activities.

# Chapter 5: The effect of pine waste and pine-biochar on nitrate mobility in biosolids

This chapter has been published. Some repetition of material from chapter 1-3 occur. Additionally, I have added photographs and other details related to this chapter in appendix

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## 5.1 Abstract

Humanity produces approximately 27 kg of dry matter in biosolids per person per year. Land application of biosolids can improve crop production and remediate soils but may result in excessive nitrate-N ($NO_3^-$-N) leaching. Carbonaceous materials can reduce the environmental impact of biosolids application. I aimed to ascertain and compare the potentials for *Pinus radiata* sawdust derived biochars and raw sawdust to reduce $NO_3^-$-N leaching from biosolids. We used batch sorption experiments 1:10 ratio of material to solution (100 mg/kg of $NH_4^+$ or $NO_3^-$) and column leaching experiments with columns containing biosolids (2.7% total N, 130 mg/kg $NH_4^+$ and 1350 mg/kg $NO_3^-$) mixed with either soil, biochar, or sawdust. One type of low temperature (350 $^oC$) biochar sorbed 335 mg/kg $NH_4^+$, while the other biochars (400 and 550 $^oC$) and sawdust sorbed <200 mg/kg $NH_4^+$. None of the materials sorbed $NO_3^-$. Biochar added at rates 20% - 50% reduced $NH_4^+$-N (<1% of total N) leaching from columns by 40 – 80%. Nitrate leaching (<7% of total N) varied little with biochar form or rate but was reduced by sawdust. Incorporating dried sawdust with biosolids showed promise to mitigate $NO_3^-$-N leaching. This effect is likely due to sorption into the pores of the biochar combined with denitrification and/or immobilization of N rather chemical sorption onto surfaces.

*Keywords: ammonium; biowastes; degraded soil; leaching; sawdust; sewage sludge*

## 5.2 Introduction

Humanity produces approximately 27 kg of biosolids (treated sewage sludge) per person per year (Hue, 2014). Applying biosolids to productive land improves plant growth (Ronald et al., 2008) but may result in both high levels of nitrate ($NO_3^-$) leaching (Correa et al., 2006b) and contamination of the soil and food chain. The application of biosolids to prime agricultural land is still unacceptable to many stakeholders even though many countries have guidelines to manage their environmental impacts. As a consequence, many biosolids are disposed of in

landfills, into waterways, or burned. This represents a waste of organic matter and plant nutrients.

Soil degradation is a common problem in most countries. In New Zealand, thousands of hectares of land, formally under Monterey pine (*Pinus radiata*) plantations, have both low soil organic matter levels and soil fertility (Eckehard et al., 2005). Similarly, land affected by open-cast mining often fails to develop a vegetative cover and requires remediation. In both cases, biosolids have been used to successfully re-establish soil fertility (Lee et al., 2003; Novak et al., 2009). However, to achieve a meaningful increase in soil organic matter, high rates (>50 t/ha) of biosolids are required. Given that biosolids comprise 2 – 5% nitrogen (N) by weight (Lee et al., 2001), rebuilding degraded soil can result in N rates of up to 2500 kg/ha, which is well in excess of the maximum rates currently permitted (ca. 200 kg N/ha/year) in most jurisdictions (EPA-VA, 2004; NZWWA, 2003). Most of the N in biosolids is in an organic form and as it mineralizes it provides a source of plant available inorganic-N that promotes plant growth with minimal N leaching. However, biosolids can also contain significant amounts of inorganic-N as ammonium ($NH_4^+$-N), which can rapidly nitrify to form $NO_3^-$-N. In aged biosolids, $NO_3^-$-N may also be present at significant levels (Smith et al., 1998). In both cases $NO_3^-$-N may be leached. Excessive loadings of mineral N are associated with high levels of $NO_3^-$-N leaching, which can contribute to eutrophication of lakes, rivers, and groundwater (Davis, 2014) and thus, should be prevented.

Mixing carbonaceous substances, such as sawdust or biochar, with biosolids can offset some of the negative environmental effects of biosolids addition (Knowles et al., 2011; Lee et al., 2001; Schmidt, 1996; Simmler et al., 2013). Composting biosolids with sawdust can reduce $NO_3^-$ leaching (Tarek et al., 2012). The timber industry produces large volumes of wood waste, including sawdust, which is often inappropriately disposed of in wood-waste piles (Robinson, 2007; Wendong et al., 2005). Provided the sawdust is not contaminated with timber treatment residues, such as copper, chromium and arsenic (CCA), this waste material may potentially be

used to improve environmental outcomes from biosolids-amended soils. Costs would be greatly reduced if the sawdust could be incorporated with the biosolids on site (degraded land, where sawdust waste accumulated), rather than being composted beforehand. However, it is unclear whether un-composted mixtures are effective in mitigating $NO_3^-$-N leaching. Composting of biosolids may improve quality of organic matter, which in turn may be beneficial for soil (Bernal et al., 2009). Furthermore, composting can reduce the amount of potentially phytotoxic compounds (Borchard et al., 2014). Thus, applying biosolids directly into soil may reduce treatment costs, but may risk negative effects on soil health and crop growth that increase costs.

Potentially, $NO_3^-$-N leaching could also be reduced by pyrolyzing pine waste and using the resulting biochar as a biosolids amendment. The sorptive properties of biochar are profoundly affected by the source material, the pyrolysis temperature (Glaser et al., 2002), the particle size (Kwapinski et al., 2010) and the degree of weathering the biochar has undergone in the soil (Novak et al., 2009). Steam activation of biochar can change the sorptive properties of biochar (Borchard et al., 2012). Ducey et al. (2013) showed that steam activation of biochars increased the microbiological communities in the soil. Fungo et al. (2014) reported that steam activation of biochar derived from *Eucalyptus* wood increased the biochar's capacity to suppress $CH_4$ and $N_2O$ emissions from soil.

Amending biosolids with biochar has been shown to reduce $NO_3^-$-N leaching from pasture by over 50% (Knowles et al., 2011), when the biochar was made from *Pinus radiata* pyrolyzed at 350$^o$C. Other authors using the same biochar, have also reported lower concentrations of $NO_3^-$-N in pasture soils following the application of ruminant urine (Taghizadeh-Toosi et al., 2011).

Reductions in soil $NO_3^-$-N leaching following biochar amendment to soils have been reported to range from 10 to 96% with results varying widely due to experimental conditions, applied N form, N and biochar rates used, biochar feedstock variations and pyrolysis temperatures (Guo et al., 2014; Knowles et al., 2011; Sika & Hardie, 2014; Troy et al., 2014).

It is unclear why biochar amendment of biosolids reduced $NO_3^-$-N leaching, it was speculated that biochar could adsorb $NH_4^+$-N or $NO_3^-$-N, thus rendering it less available for leaching and plant uptake, or that it inhibited either the mineralization of organic-N or nitrification (Knowles et al., 2011).

We hypothesized that mixing biosolids with either pine wood-waste or biochar would reduce the mobility of $NO_3^-$-N and $NH_4^+$-N. I aimed to determine the potential ability of *Pinus radiata* wood-waste and various wood-waste -derived biochars to immobilize-N in biosolids and biosolids-amended soils.

## 5.3 Materials and Methods

Soil (Lismore Stony Silt Loam), was collected (0 -30 cm) from the Lincoln University Ashley Dene sheep farm (43°39′05.82″S 172°19′41.47″E), New Zealand. The soil is a low-fertility Lismore soil formed from gravel glacial outwash with a variable depth of silty loess deposited at the surface. The soil is well drained and has moderate to rapid permeability (WRC, 2011). The soil was air-dried to a gravimetric moisture content ($\theta_g$) of 11.85% and sieved to <2 mm. Table 5.1 gives the chemical properties of the soil. Biosolids were obtained from the Kaikōura Regional treatment works (42°21′47.78″S 173° 41′20.32″E), New Zealand. Some 160 kg of stockpiled and weathered biosolids were collected and homogenized using a concrete mixer and initially passed through a 20 mm sieve. A 2 kg sub-sample was passed through a 2 mm nylon sieve. Biosolids $\theta_g$ equalled 53%. Table 5.1 gives the properties of the biosolids.

Untreated pine sawdust was obtained from a local sawmill (Shands Road Sawmills Ltd), New Zealand. After drying at 60°C to a constant weight, the sawdust was sieved to <4 mm. A further portion of the sawdust was kept moist ($\theta_g$ = 25%), as collected. The dried sawdust was pyrolyzed at a range of temperatures for varying lengths of time to produce biochars with contrasting properties. A slow pyrolysis method was used to produce low temperature biochars (350°C). A muffle furnace was used to manufacture biochars at 350°C in a low oxygen environment (Zhang et al. (2015). Sawdust (200 g) was weighed into steel containers covered

with aluminum foil. The temperature was monitored using a thermocouple to ensure the temperature of the material was maintained at 350$^{o}$C. Chars were prepared with pyrolysis times of 3 hr and 12 hr. The target temperature, 350$^{o}$C, was reached at the rate of 16$^{o}$C/min. Higher temperature biochars (400$^{o}$C and 550$^{o}$C ) were produced using a specialized furnace (Hina et al., 2010) equipped with a rotating cylinder of 5 L capacity. Liquefied petroleum gas was used as the heat source to pyrolyze the sawdust at 400$^{o}$C and 550$^{o}$C. The target temperatures were reached at rates of 38$^{o}$C/min and 46$^{o}$C/min, respectively. Treatments were prepared with and without steam activation. Steam activation, henceforth denoted as "A" was achieved by injecting water into the pyrolysis chamber at a rate of 4 mL/min with an airflow of 10 L/min. A further biochar was also made from pine at 350$^{o}$C, as previously described by Knowles et al. (2011). This biochar, contained particles sizes from <1 – 45 mm and was sieved (<4 mm) and is subsequently referred to as "bulk biochar" Table 5.1 and Table 5.4 shows the properties of the sawdust and biochars.

Table 5.1. Chemical properties of the materials used in the experiments. Values represent the mean (n=3) except pH (median). Values in brackets are the standard error. Concentrations of other elements can be found in the supplementary data. nd=not determined (because of its negligible N content).

| | pH ($H_2O$) | CEC ($cmol_c/kg$) | Bulk density ($g/cm^3$) | C (%) | N (%) | C/N ratio | $NH_4^+$ (mg/kg) | $NO_3^-$ (mg/kg) |
|---|---|---|---|---|---|---|---|---|
| Lismore stony silt loam | 6.3 | 13.5 (0.2) | 1.1 | 4.3 (0.1) | 0.37 (0.01) | 11.6 | 7.9 (2.9) | 181 (10.8) |
| Biosolids | 4.5 | 16.7 (0.7) | 0.7 | 25.3 (0.4) | 2.7 (0.0) | 9.4 | 130 (7.3) | 1352 (2.5) |
| *Pinus radiata* (pyrolysis temperature, time) A=steam activation | | | | | | | | |
| Sawdust (SD,unpyrolyzed) | 5.7 | 10.6 | 0.2 | 51 (0.04) | 0.06 (0.00) | 850 | nd | nd |
| Char 350°C, 3hr | 5.5 | 2.2 | 0.2 | 71 (0.09) | 0.03 (0.00) | 2367 | nd | nd |
| Char 350°C, 12hr | 5.5 | 1.3 | 0.2 | 72.8 (0.1) | 0.03 (0.01) | 2427 | nd | nd |
| Bulk biochar 350°C | 6.9 | 9.1 | 0.2 | 78.1 (0.08) | 0.06 (0.20) | 1302 | nd | nd |
| Char 400°C A | 6.2 | 5.9 | 0.1 | 75.5 (0.07) | 0.04 (0.00) | 1888 | nd | nd |
| Char 400°C | 5.9 | 5.2 | 0.2 | 75.3 (0.07) | 0.04 (0.00) | 1883 | nd | nd |
| Char 550°C A | 8.1 | 6.7 | 0.1 | 88.4 (0.1) | 0.03 (0.00) | 2947 | nd | nd |
| Char 550°C | 7.9 | 6.7 | 0.1 | 86.5 (0.06) | 0.03 (0.00) | 2883 | nd | nd |

The pH of the materials was determined in water using a sample: water ratio (w/w) of 1:2.5 following the method of Blakemore et al. (1987). Soil carbon (C) and N concentrations were measured using an Elementar Vario MAX CN analyzer (Elementar GmbH Germany). Cation Exchange Capacity (CEC) was measured for all materials using the method described by Blakemore et al. (1987). Extractable $NH_4^+$ and $NO_3^-$ concentrations in the soil and biosolids were determined using a 2M KCl extract following the method of Blakemore et al. (1987) and Clough et al. (2001). Water soluble C (WSC) was determined using cold (20$^o$C) and hot (80$^o$C) water extracts (Ghani et al., 2003). To measure WSC 3 g of oven dried material and 30 mL of cold distilled water were placed in polypropylene centrifuge tubes on an end-over-end shaker for 30 mins and then centrifuged for 20 min at 2250 g (3300 rpm). The extracts were then decanted off and filtered through 0.45 μm cellulose nitrate membrane filters. The sample remaining in the centrifuge tube had, a further 30 mL of distilled water added before it then placed in a hot water bath at 80$^o$C for 16 hr, where after it was centrifuged and filtered as before. Total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC) concentrations of the WSC samples were measured using a TOC-5000A analyzer (Shimadzu Oceania Pty Ltd, NSW, Australia).

### 5.3.1 Batch Sorption experiments

Batch sorption experiments were carried out with all individual materials (not mixtures) using an ambient solution of 0.01M $CaCl_2$ solution containing 100 mg/L $NH_4^+$ [pH 5.1 as $(NH_4)_2SO_4$)] or $NO_3^-$ (pH 7.0 as $KNO_3$) following the method of Wang et al. (2010). Samples (20 g of dry matter) were weighed into 250 mL centrifuge tubes, replicated thrice. Controls were also performed and had no sample addition. Then 200 mL of either the $(NH_4)_2SO_4$ or $KNO_3$ solution was added and the samples were then placed on an end-over-end shaker for 6 hr. Previous experiments had indicated that this was the minimum time required for the biochar samples to equilibrate with the $NH_4^+$ solution (data not shown). Harmayani and Anwar (2012) showed that equilibrium times for biochars in batch experiments varied from 1 – 96 hours.

The effect of pH on sorption was also determined for the bulk biochar. Batch sorption experiments used bulk biochar (10 g) and the $CaCl_2$-$(NH_4)_2SO_4$ solution at a ratio of 1:10. The pH values of these mixtures were adjusted by adding 400 µL and 200 µL of 0.6M HCl to give pHs of 3.4 and 4.2. No adjustment resulted in a pH 5.1 and 450 µL of 0.03M KOH gave a pH of 5.4. To attain pH values of 6.1 and 7.1 250 µL and 750 µL of 0.3M KOH were added, respectively. After shaking (2 hr), samples were centrifuged at 3000 rpm for 10 minutes and filtered (Whatmann 52), then analyzed for residual $NH_4^+$ and $NO_3^-$ concentrations using flow injection analysis (FIA; Alpkem FS 3000 twin channel analyzer, Texas, USA).

The biosolids were not sterile. Thus a test of the potential microbial activity on sorption experiment results was performed over a 48 hr sorption experiment where the Lismore soil and bulk biochars were mixed with the $(NH_4)_2SO_4$ solution at a ratio of 1:10. Unsterilized and sterilized 5% (v/v) phenol treatments were included. Samples were again shaken on an end-over-end shaker with sub samples collected at 10 min, 6 hr, 24 hr and 48 hr intervals, with all samples analyzed for both $NH_4^+$ and $NO_3^-$ concentrations.

### 5.3.2 Column leaching experiments

Leaching columns (4 cm height × 4 cm diameter) with an internal volume of 50.3 $cm^3$, were filled with mixtures of biosolids (sieved to <2 mm), pyrolyzed or unpyrolyzed (sawdust) pine wood (sieved to < 4 mm) and quartz sand (<1 mm). Table 5.2 lists in detail the treatments with the masses of each material. There were three replicates of each treatment. The total dry matter in each column was 15 g. Column bulk densities ranged between 0.5 $g/cm^3$ and 1.5 $g/cm^3$. The volume of water in the columns at field capacity varied between 9.4 $cm^3$ (sand) and 28.9 $cm^3$ (sawdust + biosolids). Each column was irrigated daily with 5 mL of deionized water. The eluent was collected weekly and analyzed for both $NO_3^-$-N and $NH_4^+$-N concentrations using FIA. Columns were leached under laboratory conditions (20°C) for at least three months, or until the $NH_4^+$-N and $NO_3^-$-N concentrations in the eluent had stabilized at levels equal to <5% of the concentrations recorded in the initial flush.

Data were analyzed using Minitab® 16 (Minitab Inc, State College, Pennsylvania, USA). Data sets were analyzed using ANOVA with Fisher's Least-Significant-Difference post-hoc test to compare means. The level of significance was 0.05. (*NOTE: See* **Appendix A** *for more laboratory experimental setup).*

Table 5.2. Masses (g) of materials (fresh weight) used in the column experiments. The percentage DM of each material is given in brackets following the name.

| Treatment | | Other material | | | pH of effluent | Total N (mg) | Initial $NH_4^+$-N (mg) | Initial $NO_3^-$ -N (mg) | Total $NH_4^+$-N (mg) leached | Total $NO_3^-$ -N (mg) leached |
|---|---|---|---|---|---|---|---|---|---|---|
| | Mass of treatment material | Quartz sand (>99%) | Lismore silt loam (88.2%) | Biosolids (47%) | | | | | | |
| Sand control | 0 | 15 | 0 | 0 | 5.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| Soil control | 0 | 0 | 15 | 0 | 5.2 | 48.9 | 0.2 | 0.8 | < 0.1 | 2.5 (0.2) |
| Biosolids control | 0 | 10 | 0 | 5 | 4.7 | 63.5 | 0.2 | 0.7 | 0.6 (0.00) | 3.4 (0.09) |
| Soil +Biosolids | 0 | 0 | 10 | 5 | n/d | 79.8 | 0.3 | 1.0 | 0.7 (0.03) | 6.4 (0.10) |
| Sawdust (SD, unpyrolyzed) (>99%) | 1 | 9 | 0 | 5 | n/d | 64.0 | 0.2 | 0.7 | 0.5 (0.03) | 2.8 (0.07) |
| | 2 | 8 | 0 | 5 | n/d | 64.5 | 0.2 | 0.7 | < 0.1 | 2.1 (0.1) |
| | 4 | 6 | 0 | 5 | n/d | 65.6 | 0.2 | 0.7 | < 0.1 | 1.3 (0.1) |
| | 5 | 5 | 0 | 5 | 5.1 | 66.2 | 0.2 | 0.7 | 0.2 (0.02) | 0.7 (0.1) |
| | 5 | 10 | 0 | 0 | 6.0 | 2.7 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| | 3 | 0 | 7 | 5 | n/d | 86.3 | 0.3 | 1.1 | < 0.1 | 1.8 (0.2) |
| | 5 | 0 | 5 | 5 | n/d | 79.8 | 0.3 | 1.1 | < 0.1 | 0.8 (0.2) |
| Sawdust (SD unpyrolyzed) (75%) | 5 | 10 | 0 | 0 | 6.3 | 1.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| | 5 | 5 | 0 | 5 | 5.3 | 64.6 | 0.2 | 0.7 | 0.1 (0.02) | 0.9 (0.03) |
| Char 350° C, 3hr (>99%) | 5 | 10 | 0 | 0 | 7.2 | 1.5 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| | 5 | 5 | 0 | 5 | 6.1 | 64.9 | 0.2 | 0.7 | 0.1 (0.0) | 4.0 (0.08) |
| Char 350° C, 12hr (>99%) | 5 | 10 | 0 | 0 | 7.2 | 1.5 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| | 5 | 5 | 0 | 5 | 6.4 | 64.9 | 0.2 | 0.7 | 0.1 (0.03) | 4.0 (0.2) |
| Bulk biochar 350°C | 1 | 9 | 0 | 5 | 5.7 | 64.0 | 0.2 | 0.7 | 0.3 (0.0) | 3.9 (0.2) |
| | 2 | 8 | 0 | 5 | 6.0 | 64.5 | 0.2 | 0.7 | 0.3 (0.03) | 4.0 (0.4) |
| | 3 | 7 | 0 | 5 | 6.6 | 65.1 | 0.2 | 0.7 | 0.2 (0.0) | 3.9 (0.2) |
| | 4 | 6 | 0 | 5 | 6.6 | 65.7 | 0.2 | 0.7 | 0.2 (0.01) | 4.2 (0.1) |
| | 5 | 5 | 0 | 5 | 6.8 | 66.3 | 0.2 | 0.7 | 0.2 (0.01) | 4.2 (0.3) |
| | 5 | 10 | 0 | 0 | 7.0 | 2.8 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| Char 400°C A (>99%) | 5 | 10 | 0 | 0 | 6.7 | 2.0 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| | 5 | 5 | 0 | 5 | 6.2 | 65.4 | 0.2 | 0.7 | 0.4 (0.03) | 4.2 (0.2) |
| Char 400°C (>99%) | 5 | 10 | 0 | 0 | 7.5 | 2.0 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| | 5 | 5 | 0 | 5 | 6.4 | 65.4 | 0.2 | 0.7 | 0.3 (0.05) | 3.3 (0.2) |
| Char 550°C A (>99%) | 5 | 10 | 0 | 0 | 6.3 | 1.5 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| | 5 | 5 | 0 | 5 | 6.1 | 64.9 | 0.2 | 0.7 | 0.4 (0.0) | 4.0 (0.1) |
| Char 550°C (>99%) | 5 | 10 | 0 | 0 | 7.2 | 1.4 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| | 5 | 5 | 0 | 5 | 6.4 | 64.9 | 0.2 | 0.7 | 0.7 (0.0) | 4.4 (0.2) |

Table 5.3. Dissolved organic carbon of each materials. Values represent the mean (n=3) and values in brackets are the standard error.

| Materials | Total Organic carbon (TOC) mg/kg | |
|---|---|---|
| | Cold water extract | Hot water extract |
| Lismore stony silt loam | 382 (2) | 728 (17) |
| Unpyrolyzed pine sawdust | 6063 (21) | 5150 (14) |
| Pine char 350ºC, 3 hr | 462 (20) | 1043 (57) |
| Pine char 350ºC, 12 hr | 375 (6.2) | 431 (16) |
| Bulk biochar 350ºC | 1468 (28) | 3054 (137) |
| Pine char 400ºC A | 1182 (89) | 1876 (34) |
| Pine char 400ºC | 1300 (20) | 2054 (72) |
| Pine char 550ºC A | 833 (75) | 407 (7) |
| Pine char 550ºC | 150 (7) | 339 (9) |

Table 5.4. Plant macronutrients in the materials used in the experiments. All concentrations in mg/kg Values represent the mean (n=3).

| | Na | K | Ca | Mg | S | P |
|---|---|---|---|---|---|---|
| Lismore stony silt loam | 160 (15.7) | 2330 (102) | 5392 (215) | 1638 (18) | 487 (5.2) | 991 (21) |
| Biosolids | 299 (21) | 3014. (173) | 9455 (54) | 2994 (55) | 6736 (450) | 3463 (248) |
| ***Pinus radiata* (pyrolysis temperature, time) A=steam activation** | | | | | | |
| Unpyrolyzed sawdust | 964 (67) | 921 (6.8) | 1059 (29) | 443 (2.9) | 87.1 (0.1) | 49.5 (0.06) |
| Char 350°C, 3 hr | 762 (20.8) | 1400 (48.7) | 1667 (92) | 511 (23.4) | 107 (3.4) | 79.3 (4) |
| Char 350°C, 12 hr | 1620 (17.6) | 2211 (7.8) | 3012 (31.9) | 889.2 (1.8) | 160.9 (1.5) | 148.1 (1.5) |
| Char 350°C (bulk biochar) | 2504 (15) | 4795 (16.6) | 37767 (66) | 2038 (13.5) | 1268 (11.3) | 834 (8.0) |
| Char 400°C A | 2062 (35) | 4782 (24.7) | 5530 (23) | 1723 (21) | 413 (0.8) | 627 (4.9) |
| Char 400°C | 1845 (53.5) | 4443 (92.0) | 5343 (156) | 1696 (27.6) | 392 (4.4) | 587 (12.6) |
| Char 550°C A | 1965 (19.3) | 4474 (16.1) | 5097 (15.8) | 1756(4) | 272.8 (1.0) | 596 (0.6) |
| Char 550°C | 2032 (33) | 4863 (28) | 5453 (35) | 1752 (2.2) | 628 (120) | 730 (18.2) |

## 5.4 Results and discussion

### 5.4.1 Inorganic-N sorption

None of the materials tested sorbed $NO_3^-$ (data not shown). Using sugarcane bagasse as a biochar feedstock, Kameyama et al. (2012) reasoned that the increased sorption of $NO_3^-$ with increasing temperature was the result of base functional groups, on the biochar surface, increasing in number with increasing pyrolysis temperature. Wang et al. (2015) also found $NO_3^-$ sorption increased with increasing biochar manufacturing temperature. Clough et al. (2013) reviewed the studies examining $NO_3^-$ sorption on biochar and concluded that sorption of $NO_3^-$ onto a biochar surface was unlikely to occur unless the pyrolysis temperature during biochar manufacture was >600ºC, with the degree of $NO_3^-$ sorption also dependent on feedstock type. Other more recent studies, also showing low sorption of $NO_3^-$ by biochar, have generally examined biochar manufactured at pyrolysis temperatures < 600ºC (Gai et al., 2014; Hale et al., 2013; Zhang et al., 2015). Thus, ignoring feedstock type as an issue, the lack of $NO_3^-$ sorption in the current experiment is most likely a result of the relatively low pyrolysis temperatures, used to manufacture the biochar materials, preventing base functional group formation. Sawdust materials can retain cations but they are not able to bind anions unless they are chemical modified (Ebrahimi & Roberts, 2013; Keränen et al., 2015; Mishra & Patel, 2009; Sousa et al., 2010; Su et al., 2012). Given these results it can be concluded that neither the biochars nor the sawdust will reduce $NO_3^-$ leaching via $NO_3^-$ sorption mechanisms occurring.

In contrast, all of the materials tested with the exception of pine sawdust, sorbed significant amounts of $NH_4^+$ ranging from 14 to 335 mg $NH_4^+$/kg material (Figure 5-1). However, only the biochar produced at 350ºC, for 12 hr, and the "bulk biochar" sorbed more $NH_4^+$ than the soil on its own ($p < 0.05$). The amounts of $NH_4^+$ sorbed by the biochars in the current study were relatively small compared to previous reports. For example, Sarkhot et al. (2013), reported biochar produced from hardwood shavings, pyrolyzed at 300ºC, sorbed up to 5300 mg $NH_4^+$/kg. Differences in biochar sorptive capacity for $NH_4^+$ have been shown to result

from feedstock type, for example, *Thalia sp*. and *Schinus sp.* have been shown to sorb $NH_4^+$ up to 785 mg/kg and 3700 mg/kg by Yao et al. (2012) and Zeng et al. (2013) respectively.

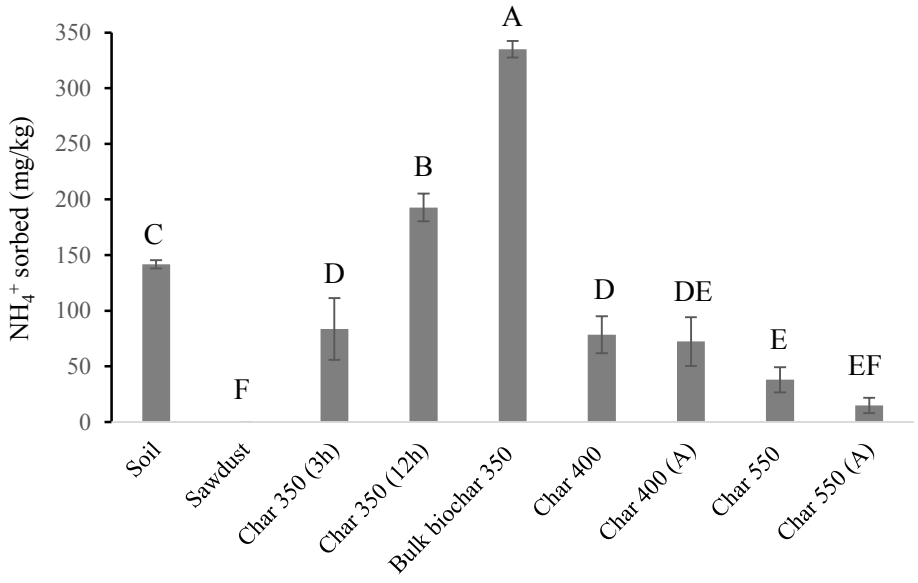


Figure 5-1. $NH_4^+$ sorbed (mg/kg) dry weight by soil, sawdust and biochar from a 100 mg/L $NH_4^+$ solution after 6 hr of agitation. Material: solution ratio 1:10. Bars represent the standard error of the mean (n=3). Bars with the same letter are not significantly different.

Biochar retention of $NH_4^+$ is a function of the materials' CEC, which besides being a function of feedstock type, is also the result of the biochar production method. Specifically, the CEC of a biochar is a function of the biochar pH which varies with pyrolysis temperature. This was demonstrated by Lehmann et al. (2007), using *Robinia pseudoacacia* as a feedstock, who showed a strong correlation between increasing biochar pH and increasing CEC as the pyrolysis temperature was increased, with an optimal CEC of 20 $cmol_c$/kg at a temperature of 450$^o$C and pH ~ 9. Similar results were observed by Zhang et al. (2015) for *Quercus sp*. In the current study increasing the pH during the batch sorption experiments also increased the sorption of $NH_4^+$ (Figure 5-2) and this is consistent with the surface charge varying with pH and directly influencing the biochar's CEC (Lehmann, 2007).

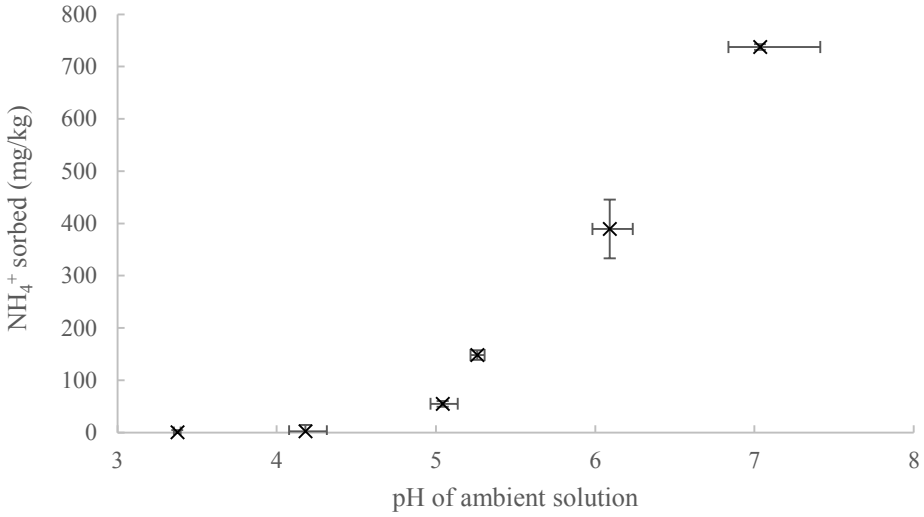


Figure 5-2. $NH_4^+$ sorbed (mg/kg) dry weight by the "bulk biochar" from a 100 mg/L $NH_4^+$ solution after 2 hr of agitation at various solution pH values. Material: solution ratio 1:10. Bars represent the standard error of the mean (n=3)

Other studies specifically measuring CEC following the pyrolysis of *Pinus sp.,* at 400ºC and 600ºC, have shown CEC to range from 10-38 $cmol_c$/kg at near neutral biochar pH (Mukherjee et al., 2011). The lower CEC values in this range are consistent with the lower CEC values for the materials in the current study (Table 5.1). For non *Pinus sp.,* the range is reported as 0.2 – 25 $cmol_c$/kg and varies with different feedstock and pyrolysis conditions (Cheng et al., 2006; Gundale & DeLuca, 2007; Lehmann, 2007; Nguyen & Lehmann, 2009; Sarkhot et al., 2013). In the current study there was no significant correlation ($r$=0.19: $p$>0.05) between the CEC of the materials tested and their ability to sorb $NH_4^+$. Sterilizing the solutions during the batch sorption experiments showed no significant differences occurred in terms of $NH_4^+$ sorption. This observation and the lack of any increase in the $NO_3^-$ concentration (results not shown) indicates that microbial activity did not affect the results of our batch-sorption experiments.

The lack of any significant sorption of $NH_4^+$ by the sawdust may be due to several reasons. Sawdust cell walls are active ion exchange sites due to the presence of cellulose, lignin and hydroxyl groups (Shukla et al., 2002). However, cation adsorption onto sawdust is pH

dependent, in the case of heavy metals, and thus in the current study lack of $NH_4^+$ sorption may be due to non-optimum pH conditions for maximum CEC expression. Another factor that prevents cation exchange on sawdust includes competition for cation sorption sites. In the current study the $Ca^{2+}$ ions in the assay matrix may have competed with $NH_4^+$and been selectively adsorbed on the sawdust (Shukla et al., 2002). Furthermore, Harmayani and Anwar (2012) found the initial cation concentrations and extraction time also affected sorption onto *Pinus* sawdust. Thus these factors may not have been optimal in the current study for sorption of $NH_4^+$ by sawdust. Based on these results the sorption of $NH_4^+$ is not a mechanism that will reduce the potential leaching of $NO_3^-$ when mixing biosolids with biochars or sawdust and soil.

### 5.4.2 Inorganic-N leaching from the column study

Ammonium-N in the leachate accounted for <1% of N applied (Figure 5-3). The assumption is made that, given the N content of the biochar, the source of the $NH_4^+$-N in the leachate is the biosolids (Table 5.1). When biochar materials were mixed with biosolids in the leaching columns, the biochars reduced the amount of $NH_4^+$-N leached when expressed as a percentage of the total –N initially present in the biosolids (Figure 5-3 and Figure 5-5). The effect of increasing biochar rate, observed with the bulk biochar treatment, was to further reduce $NH_4^+$ leaching. This is, most likely, a consequence of the increasing CEC, since the amount of $NO_3^-$-N leached did not vary with the bulk biochar rate applied (Figure 5-4). This also indicates that increasing the rate of biochar addition did not significantly accelerate nitrification, via potential liming effects, which could in turn have enhanced subsequent $NO_3^-$-N leaching (Clough et al., 2013). Incorporating biochar into acidic agricultural soils, accelerates nitrification and thus weakens the liming effects of biochar (Zhao et al., 2014).

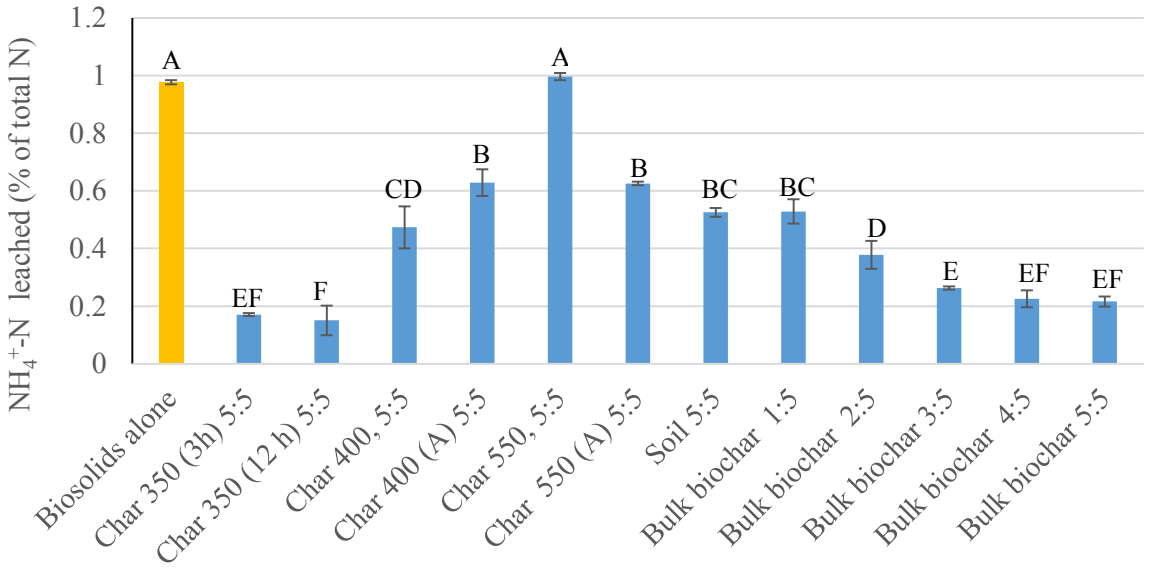


Figure 5-3. $NH_4^+$-N leached (as a % of total N in the columns), from columns with the materials described in Table 5.2 mixed with biosolids. Number ratios indicate the mass of material (g): mass of biosolids (g). Bars represent the standard error of the mean (n=3).

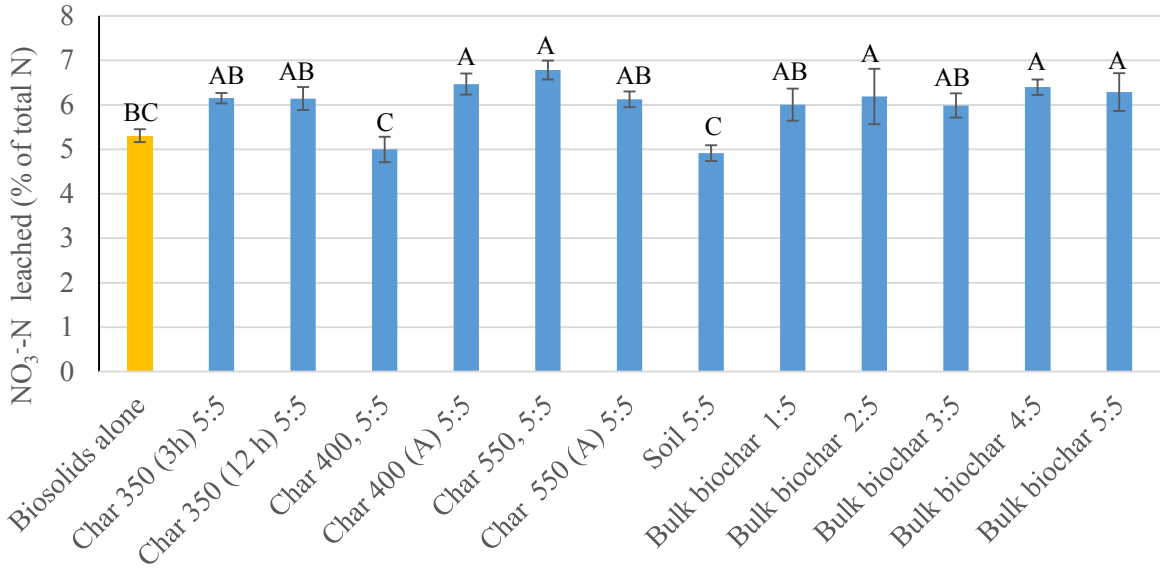


Figure 5-4. $NO_3^-$-N (as a % of total N in the columns), from columns with the materials described in Table 5.2 mixed with biosolids. Number ratios indicate the mass of material (g): mass of biosolids (g). Bars represent the standard error of the mean (n=3).

The low temperature biochars (350°C) reduced $NH_4^+$-N leaching more than the high temperature chars (400 and 550°C), while steam activation did not have a consistent effect on

$NH_4^+$-N leaching (Figure 5-3). Park et al. (2003) and Shafeeyan et al. (2010) reported that although steam activation increased the surface area and micropore volume of biochar, it depleted the surface functional groups, possibly offsetting any increase in sorption capacity.

Another possible mechanism for reducing $NH_4^+$-N leaching declining with increasing biochar rate is microbial immobilization of $NH_4^+$. The C:N ratios of most of our biochar: biosolids and sawdust: biosolids mixtures (calculated from Table 5.1) were above 25, the value required to trigger immobilization (McLaren & Cameron, 1996). Another possibility for reducing $NH_4^+$-N leaching could be due to the release of $N_2O$ via nitrification process, however, $N_2O$ emission was not studied. I did not measure any microbiological parameters, however, if there were significant microbial immobilization, then there would be a negative correlation between WSC (Table 5.3) and the mass of $NH_4^+$-N leached (Figure 5-3 and Figure 5-5). However, the hot and cold WSC concentrations did not correlate with the reduction in $NH_4^+$-N leaching observed ($r$ =-0.35 $P$>0.05 NS). reduction in $NH_4^+$-N leaching observed ($r$ =-0.35 $P$>0.05 NS). While $NH_3$ adsorption onto biochar can occur (Taghizadeh-Toosi et al., 2011) the likelihood of $NH_3$ adsorption occurring in the biochar material, as a mechanism for reducing $NH_4^+$ in solution, is unlikely due to the pH being too low <7.0. The different pH values of the solutions in our batch sorption experiments ranged from 4.2 – 5.8.

Nitrate leaching from the column experiment accounted for <7% of the N applied (Figure 5-4) and showed few differences as a consequences of biochar/biosolids treatment. Most of the N in the biosolids remained as organic N. None of the biochar treatments caused a significant decrease in $NO_3^-$-N leaching (Figure 5-4) in fact the high temperature biochars and the high rates of the "bulk biochar" caused an increase ($p$ <0.05) in $NO_3^-$-N leaching. Reasons for the greater $NO_3^-$-N leaching could include greater aeration of the biosolids material, resulting in higher rates of mineralization and subsequent nitrification causing more $NO_3^-$-N leaching. Our result deviates from the findings of Knowles et al. (2011) who reported that the bulk biochar significantly reduced $NO_3^-$-N leaching from biosolids-amended soil. However, the

experimental conditions described in Knowles et al. (2011) were significantly different. Their experiment was carried in the field with large lysimeters containing intact soil cores with pasture present (*Lolium perenne* L.), and thus plant N uptake.

Polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOC's) may be present in biochars and sawdust (Spokas et al., 2011) and can potentially reduce nitrification (Clough et al., 2010) and/or mineralization (Steiner et al., 2008) demonstrated that VOCs from biochar influence N-cycle and can reduce greenhouse gas emissions from soil. The fact that the $NO_3^-$-N leached, as a percentage of N applied, was higher ($p$ <0.05) under the biochar treatments than in the biosolids alone (Figure 5-4) indicates that if biochar-borne VOCs were inhibiting nitrification, then the effect was small.

Sawdust caused a significant reduction ($p$ <0.05) in both $NH_4^+$-N and $NO_3^-$-N leaching from both biosolids and biosolids-amended soil treatments (Figure 5-5 and Figure 5-6). Rates >2 parts of sawdust to 5 parts of biosolids eliminated $NH_4^+$-N leaching and reduced $NO_3^-$-N leaching by >40% (Figure 5-6). These results cannot be explained by chemical sorption mechanisms because the batch experiments revealed that the sawdust sorbed neither $NH_4^+$-N nor $NO_3^-$-N. Adding sawdust increased the C:N ratio (Table 5.1) of the mixtures, which may have resulted in microbial immobilization of biosolids derived N. The sawdust's C:N ratio of 850 is well in excess of the value required to trigger immobilization (C:N ~ >25:1 McLaren and Cameron (1996).

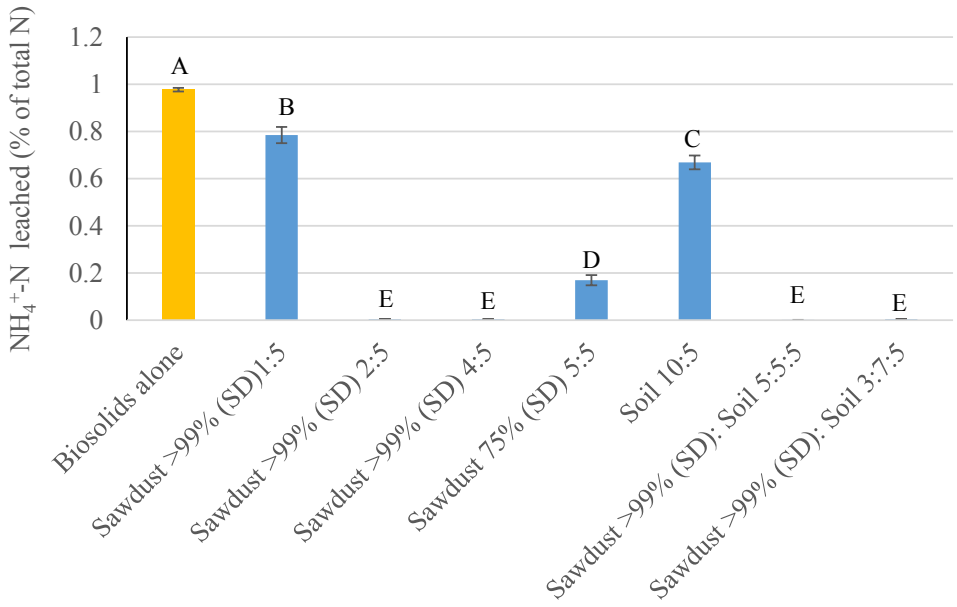


Figure 5-5. $NH_4^+$-N leached, (as a % of total N in the columns), from columns with the materials described in Table 5.2 mixed with biosolids. Number ratios indicate the mass of material (g): mass of biosolids (g). Bars represent the standard error of the mean (n=3).

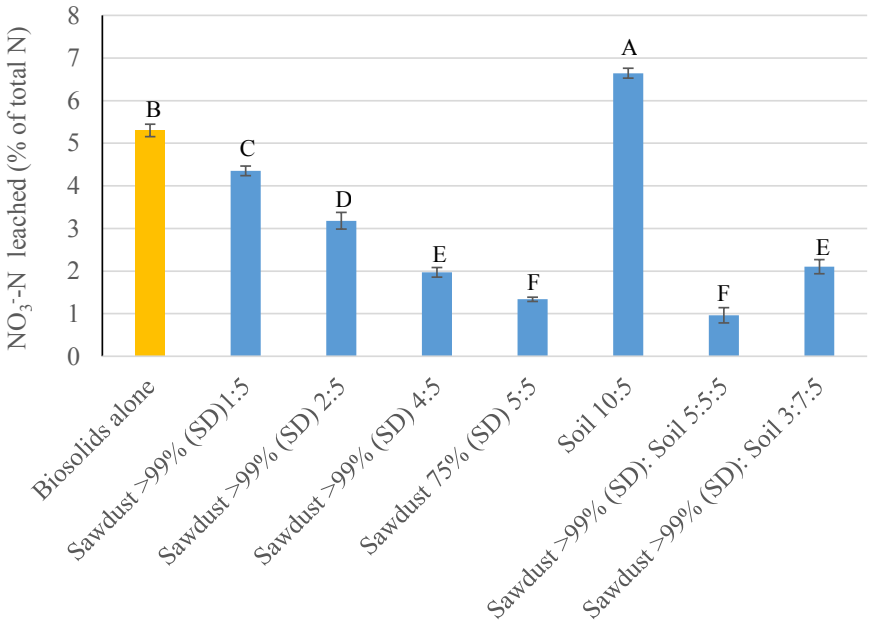


Figure 5-6. $NO_3^-$-N leached (as a % of total N in the columns), from columns with the materials described in Table 5.2 mixed with biosolids. Number ratios indicate the mass of material (g): mass of biosolids (g). Bars represent the standard error of the mean (n=3).

The WSC extracts (Table 5.3) also show that C was readily available for microbial immobilization to occur. Consistent with this theory are the results of Lee et al. (2001) who showed that adding sawdust to biosolids at a rate of 3:2 reduced $NO_3^-$-N in soil pore water by over 50%. In contrast, Schmidt (1996) showed that a 1:1 biosolids: sawdust mixture was ineffective in reducing $NO_3^-$-N leaching in the first growing season. The high WSC availability also raises the possibility of other heterotrophic activity, such as denitrification, also consuming $NO_3^-$-N and contributing to the decrease in $NO_3^-$-N leaching observed. Schipper and Vojvodic-Vukovic (1998) showed that soil amended with sawdust will remove $NO_3^-$-N from the groundwater via denitrification. Sawdust with a moisture content of 25% had a significantly smaller effect on $NH_4^+$-N and $NO_3^-$-N leaching than dry sawdust (Figure 5-5 and Figure 5-6). This indicates that the sawdust may have irreversibly sorbed some of the N-rich pore water from the fresh biosolids and that physical sorption may be an important mechanism for the retention of N in these experiments. This experiments did not provide any information on the mechanisms of such physical sorption. Biochar containing some partially pyrolyzed or unpyrolyzed material may therefore also mitigate N leaching. In this case, partial pyrolysis may be a low-cost means of drying the material. As the material weathers in the soil, the CEC of the biochar may increase (Glaser et al., 2002; Liang et al., 2006), further retaining $NH_4^+$-N in the root-zone, where plant uptake can occur.

## 5.5 Conclusion

The potential for unweathered biochars, derived from sawdust feedstock, to mitigate $NO_3^-$-N leaching from biosolids-amended soils is low and the biochars may even accelerate $NO_3^-$-N leaching. However, pine waste and pine-biochars significantly reduced $NH_4^+$-N mobility. Conversely, including raw dried sawdust when amending soils with biosolids shows significant promise to limit N-mobility in biosolids and potentially reduce $NO_3^-$-N leaching. Future work should look to better understand the reasons for this while optimizing rates and methods to achieve $NO_3^-$-N leaching mitigation.

# Chapter 6: The effect of lignite on nitrogen mobility in a low-fertility soil amended with biosolids and urea

This chapter has been published. Some repetition of material from chapters 1-3 and 6 chapters. This Chapter 6 includes a part of Anna Carlton BSc (Honors), $N_2O$ research work collaboratively carried out at the same lysimeter facilities and treatments of the current study (additional photographs and other details related to this chapter are in appendix).

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## 6.1 Abstract

Lignite has been proposed as a soil amendment that reduces nitrate ($NO_3^-$) leaching from soil. Our objective was to determine the effect of lignite on nitrogen (N) fluxes from soil amended with biosolids or urea. The effect of lignite on plant yield and elemental composition was also determined. Batch sorption and column leaching experiments were followed by a lysimeter trial where a low fertility soil was amended with biosolids (400 kg N/ha equivalent) and urea (200 kg N/ha equivalent). Treatments were replicated three times, with and without lignite addition (20 t/ha equivalent). Lignite did not reduce $NO_3^-$ leaching from soils amended with either biosolids or urea. While lignite decreased $NO_3^-$ leaching from an unamended soil, the magnitude of this effect was not significant in an agricultural context. Furthermore, lignite increased cumulative $N_2O$ production from soils receiving urea by 90%. Lignite lessened the beneficial growth effects of adding biosolids or urea to soil. Further work could investigate whether coating urea granules with lignite may produce meaningful environmental benefits.

*Keywords:* black urea; coal; fertilizer; lysimeter; sewage sludge

## 6.2 Introduction

Countries with sewage treatment plants produce approximately 27 kg (dry mass) of biosolids (sludge) per person per year (Hue, 2014). Biosolids can be used to rebuild low-fertility or degraded soils (Rigby & Smith, 2013; Robinson et al., 2011), but may have detrimental effects through contributing to nitrate ($NO_3^-$) leaching (Correa et al., 2006b) and due to accumulation of heavy metals in both soils and plants (Civeira & Lavado, 2008). Most nitrogen (N) in biosolids is present as organic N, which only oxidises slowly, but there are often high concentrations of ammonium ($NH_4^+$) and $NO_3^-$ (Correa et al., 2006a). This can result in a large flush of $NO_3^-$ leaching if sufficient rainfall occurs shortly after application. High concentrations of $NO_3^-$ in soil can also result in large emissions of nitrous oxide ($N_2O$) (Di &

Cameron, 2002b), a greenhouse gas that has a global warming potential 298 times that of $CO_2$ (Ravishankara et al., 2009).

Knowles et al. (2011) reported that $NO_3^-$ leaching from biosolids applied to soil could be mitigated by mixing the biosolids with biochar, produced by pyrolysing wood-waste. However, biochar is not available in sufficient quantities for large-scale commercial operations and thus it is currently expensive (US$200 - US$500 per ton) (Kulyk, 2012). Lignite, a low grade coal (Kabe et al., 2004) may be an alternative option for reducing $NO_3^-$ leaching from biosolids. Lignite is globally abundant with ca. $195\times10^9$ t of proven and recoverable lignite resources, (WEC, 2010) including $333\times10^6$ t located in New Zealand. Lignite has a similar structure to many biochars (Kwiatkowska et al., 2008). Hypothetically, biochar comprises 54.9% carbon (C), 2.14% hydrogen (H), 4.97% N and 20.04% oxygen (O) (Ozcimen & Karaosmanoglu, 2004), whereas lignite has 65% C, 5% H, 1.2% N and 27.8% O (Janos et al., 2011). Lignite has a greater number of organic functional groups than biochar, with a resultant higher Cation Exchange Capacity (CEC) 20 -70 $cmol_c/kg$ (Wong et al., 1996), compared to 20 -35 $cmol_c/kg$ for a typical biochar (Gundale & DeLuca, 2007). The higher CEC of lignite may provide greater retention of $NH_4^+$ and thus lower the potential for $NO_3^-$ leaching loss.

There is a paucity of scientific research examining the effects of unmodified lignite on $NO_3^-$ leaching. Commercially, however, lignite has been combined with urea ($CO(NH_2)_2$) and sold as “black urea”(Ferguson, 2002). In South Africa, van Vuuren and Claassens (2009), have reported that in pot trials and field trials the yield of *Zea mays* L. increased by 20-46% when “black urea” was applied versus standard urea. They also showed that 10-20% and 30-50% less “black urea” was required than normal urea when applied as topdressing on alkaline and acidic soils respectively. ARTH (2009) reported that the fertilizer requirements of field grown maize (*Zea mays* L) were reduced by 15 – 35% when “black urea” and “black DAP (lignite coated

di-ammonium phosphate fertilizer) were applied, compared to the uncoated fertilizers. There is little scientific validation of these claims. In contrast, there are many studies demonstrating heavy metal sorption by lignite (Domańska & Smolinska, 2012; Doskocil & Pekar, 2012; Jezierski et al., 2000). Qi et al. (2011) showed that lignite mixed with dewatered biosolids sludge could reduce heavy metal leaching. Simmler et al. (2013) also demonstrated that lignite could reduce plant cadmium (Cd) uptake from biosolids-amended soils. Lignite may also offset potentially toxic effects of high copper (Cu) and zinc (Zn) concentrations (Lafferty & Hobday, 1990) that are typically found in biosolids and which can accumulate in a soil. I aimed to evaluate the combined effect of lignite amendments on both N and trace metal mobility in a soil.

We hypothesised that incorporating lignite into soils amended with biosolids would (i) reduce N leaching as a result of increased CEC and (ii) reduce the plant uptake of heavy metals. These hypotheses were tested using batch studies, column-leaching studies and a lysimeter experiment.

## 6.3 Materials and Methods

### 6.3.1 Soil

Lismore Stony Silt Loam (NZ classification: Pallic Orthic Brown Soil) was collected (0 -30 cm depth) from the Ashley Dene sheep farm at Lincoln University (43°39′05.82″S 172°19′41.47″E), New Zealand. The low-fertility Lismore soil (Table 6.1) was formed from gravelly glacial outwash gravels and has a variable depth of silty loess deposited at the surface. The soil was air-dried to a gravimetric moisture content ($\theta_g$) of 11.9% and sieved to < 2 mm. Table 6.1 gives the chemical properties of the soil.

### 6.3.2 Biosolids

Biosolids were obtained from the Kaikōura Regional treatment works (42°21′47.78″S 173° 41′20.32″E), New Zealand. Some 160 kg of stockpiled and weathered biosolids were collected and homogenised using a concrete mixer and passed initially through a 20 mm sieve. A 2 kg sub-sample was then passed through a 2 mm nylon sieve. Biosolids $\theta_g$ equalled 53%. Table 6.1 gives the properties of the biosolids.

### 6.3.3 Lignite

Three types of powdered lignites were provided by Solid Energy New Zealand Ltd. The New Vale lignite (NV), a low calorific value lignite, was sourced from an open cast mine in Southland, New Zealand, (46°08′23.80″S 168°45′11.62″E), the Charleston lignite, was sourced from Charleston open cast mine near Charleston, West Coast, New Zealand (41°54′51.77″S 171°25′58.62″E), and the Millerton lignite, was sourced from the Millerton section of the Stockton open cast mine on the West Coast, New Zealand (41°39′47.67″S 171°51′52.17″E). The lignites were sorted on a crusher with an air swept classifier, which separated the lignite particles based on size (Simmler et al., 2013). Table 6.1 shows the chemical properties of the respective lignites.

The pH of the soil, biosolids and lignites was determined in water using a sample: water ratio (w/w) of 1:2.5 following the method of Blakemore et al. (1987) using a Mettler Toledo, GmbH, Switzerland. Carbon (C) and N concentrations were determined using an Elementar Vario MAX CN analyzer (Elementar GmbH Germany). The CEC was measured with the silverthiourea method described by Blakemore et al. (1987). Extractable $NH_4^+$ and $NO_3^-$ concentrations in the soil and biosolids were determined with a 2M KCl extract following the method of Blakemore et al. (1987) and Clough et al. (2001).

Water soluble C (WSC) was determined using cold (20°C) and hot (80°C) water extracts (Ghani et al., 2003). To measure WSC, 3 g of oven dried material and 30 mL of cold distilled

water were placed in polypropylene centrifuge tubes on an end-over-end shaker for 30 minutes and then centrifuged for 20 min at 2253 *g*. The extracts were then decanted off and filtered through 0.45 μm cellulose nitrate membrane filters. The sample remaining in the centrifuge tube had a further 30 mL of distilled water added before it was then placed in a hot water bath at 80ºC for 16 hr, where after it was centrifuged and filtered as before. Total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC) concentrations of the WSC samples were measured using a TOC-5000A analyzer (Shimadzu Oceania Pty Ltd, NSW, Australia).

Element concentrations were measured in acid digests by the ICP-OES (Varian 720-ES, Melbourne, Australia). Samples (0.5 g dry weight) of soil, lignites, biosolids or pasture (harvested from the lysimeters) were digested in 5 mL $HNO_3$ / 1 mL $H_2O_2$ (Merck hydrogen peroxide 30%) at 175ºC for 20 minutes. The digest was diluted with deionized water (Milli Q :Barnstead, EASYpure RF, 18.2 MΩ-cm) to a volume of 25 mL and filtered through a Whatman 52 filter paper (Simmler et al., 2013). A Wageningen reference soil (ISE 989) and plant (IPE 100) material were analysed for quality assurance (van Dijk & Houba, 1998).

Table 6.1. Physicochemical properties of the materials used in the experiments. Values represent the mean (n=3) except pH (median). Values in brackets are the standard error.

| | **Lismore stony silt loam** | **Biosolids** | **Lignites** | | |
|---|---|---|---|---|---|
| | | | **New Vale** | **Charleston** | **Millerton** |
| pH ($H_2O$) | 6.3 | 4.5 | 4.5 | 4.1 | 3.4 |
| Moisture % | 11.8 (0.02)$^{d}$ | 48.7 (0.008)$^{a}$ | 38 (0.36)$^{c}$ | 47.9 (0.38)$^{b}$ | 1.2 (0.002)$^{e}$ |
| $NH_4^+$(mg/kg) | 7.9 (2.9)$^{b}$ | 130 (7.3)$^{a}$ | n/a | n/a | n/a |
| $NO_3^-$(mg/kg) | 181 (10.8)$^{b}$ | 1352 (2.5)$^{a}$ | n/a | n/a | n/a |
| CEC ($cmol_c/kg$) | 12.6 (0.2)$^{d}$ | 16.7 (0.7)$^{b}$ | 43.6 (0.8)$^{a}$ | 14.7 (0.2)$^{c}$ | 2.1 (0.3)$^{e}$ |
| Base saturation (%) | 45.5(1.5)$^{c}$ | 106.9(2.3)$^{b}$ | 115.3 (0.5)$^{b}$ | 125.2 (2.5)$^{a}$ | 15.3 (4)$^{c}$ |
| Bulk density (g/cm3) | 1.1 | 0.7 | 0.6 | 0.8 | 0.7 |
| Total C (g/kg) | 48.3 (3.7)$^{e}$ | 296 (4.9)$^{d}$ | 862 (3.6)$^{a}$ | 558 (13.7)$^{b}$ | 515 (6)$^{c}$ |
| Total N (g/kg) | 3.8 (0.08)$^{d}$ | 30.7 (0.6)$^{a}$ | 12.4 (0.08)$^{b}$ | 8.7 (0.4)$^{c}$ | 9.2 (0.2)$^{c}$ |
| C/N | 12.9 (0.1)$^{d}$ | 9.7 (0.2)$^{e}$ | 69.8 (0.3)$^{a}$ | 64.5 (1.8)$^{b}$ | 56.3 (0.4)$^{c}$ |
| Water soluble carbon-cold (WSC) (mg/kg) | 382 (2)$^{b}$ | n/a | 901(30)$^{a}$ | 203 (8)$^{c}$ | 3.4 (3)$^{d}$ |
| Water soluble carbon-hot (WSC) (mg/kg) | 728 (17)$^{b}$ | n/a | 3028 (63)$^{a}$ | 1026 (4)$^{b}$ | 77 (4)$^{c}$ |
| P (mg/kg) | 991.2 (21)$^{b}$ | 3463 (248)$^{a}$ | 57.6 (0.2)$^{d}$ | 478.3 (50)$^{c}$ | 4.2 (0.3)$^{d}$ |
| S (mg/kg) | 486.7 (5)$^{c}$ | 6736 (450.2)$^{b}$ | 6539 (35)$^{b}$ | 6180 (589)$^{b}$ | 13799 (455)$^{a}$ |
| Ca (mg/kg) | 5393 (216)$^{c}$ | 9455 (534)$^{b}$ | 17502 (119)$^{a}$ | 1850 (190)$^{d}$ | 51.9 (1.1)$^{e}$ |
| Mg (mg/kg) | 1638 (68)$^{c}$ | 2994 (55)$^{a}$ | 2815 (11)$^{b}$ | 779.4 (85)$^{d}$ | 13.4 (0.8)$^{e}$ |
| K (mg/kg) | 2330 (102)$^{b}$ | 3014 (173)$^{a}$ | 219 (2)$^{c}$ | 295 (21)$^{c}$ | 30.8 (1.6)$^{d}$ |
| Na (mg/kg) | 160 (9.1)$^{b}$ | 299 (12)$^{a}$ | 176 (1.1)$^{b}$ | 94 (3.7)$^{c}$ | 69 (1.5)$^{d}$ |
| Al (mg/kg) | 23371 (865)$^{a}$ | 17351 (500)$^{b}$ | 2488 (44.7)$^{c}$ | 3629 (48.9)$^{c}$ | 134 (1.3)$^{d}$ |
| B (mg/kg) | 7.0 (0.2)$^{cd}$ | n.d | 36.3 (0.1)$^{b}$ | 211.2 (24)$^{a}$ | 23.4 (0.6)$^{bc}$ |
| Cu (mg/kg) | 7.3 (0.1)$^{b}$ | 637.3 (39)$^{a}$ | 2 (0)$^{b}$ | 3.85 (0.4)$^{b}$ | 1.9 (0.0)$^{b}$ |
| Cd (mg/kg) | 0.17 (0.001)$^{b}$ | 2.3 (0.1)$^{a}$ | 0.06 (0.007)$^{c}$ | 0.1 (0.0)$^{bc}$ | 0.04 (0.0)$^{c}$ |
| Fe (mg/kg) | 18186 (450)$^{a}$ | 8352 (221)$^{c}$ | 12918 (145)$^{b}$ | 3490 (198)$^{d}$ | 1704 (184)$^{e}$ |
| Mn (mg/kg) | 355 (1)$^{a}$ | 189 (2.2)$^{c}$ | 280 (3)$^{b}$ | 30.3 (2)$^{d}$ | 1.45 (0.1)$^{e}$ |
| Zn (mg/kg) | 81 (3)$^{b}$ | 1047 (69)$^{a}$ | 9 (1)$^{c}$ | 20 (2.2)$^{c}$ | 35.5 (1.2)$^{bc}$ |

nd – not detected : n/a –not analysed.

### 6.3.4 Batch Sorption experiments

Batch sorption experiments were carried out with the three lignites using an ambient solution of 0.01M $CaCl_2$ solution containing 100 mg/L $NH_4^+$ [pH 5.1 as $(NH_4)_2SO_4$)] or $NO_3^-$ (pH 7.0 as $KNO_3$) following the method of Wang et al. (2010). Samples (20 g of dry matter) were weighed into 250 mL centrifuge tubes, replicated thrice. Controls were prepared with no sample addition. Then 200 mL of either the $(NH_4)_2SO_4$ or $KNO_3$ solution was added and the samples were placed on an end-over-end shaker for 6 hr. Previous experiments had indicated that this was the minimum time required to reach an approximate equilibrium between the solution and the material (data not shown). Based on the sorption experiments, the NV lignite was selected for further experimentation because it had the highest CEC (Table 6.1) and showed the greatest capacity to sorb $NH_4^+$.

The effect of pH on $NH_4^+$ sorption was determined for the NV lignite. Batch sorption experiments used NV lignite (10 g) and the $CaCl_2$-$(NH_4)_2SO_4$ solution at a ratio of 1:10. The pH values of these mixtures were adjusted by adding 50 µL, 100 µL, 125 µL, 150 µL, 175 µL, 200 µL and 250 µL of 10M KOH to give pHs of 4.4, 4.9, 5.2, 5.5, 6.0, 6.3, and 6.7, respectively. After agitation, the samples were centrifuged at 3000 rpm for 10 minutes and filtered (Whatmann 52), then analysed for residual $NH_4^+$ concentrations using flow injection analysis (FIA; Alpkem FS 3000 twin channel analyzer, Texas, USA).

### 6.3.5 Column leaching experiments

Leaching columns (4 cm height × 4 cm diameter), with an internal volume of 50.3 mL, were filled with mixtures of biosolids (sieved to < 2 mm), NV lignite (< 1 mm) and quartz sand (< 1 mm) and maintained at 20°C. The total dry weight of the materials added was 30 g. The biosolids ratio (by weight) was 5 parts in each treatment, lignite was added at 0, 1, 2, 3, 4, 5 g and the total weight brought to 30 g by adding appropriate weights of quartz sand. Each column

was irrigated daily with 5 mL of deionised water. Column bulk densities ranged between 1.1 g/cm$^3$ and 1.5 g/cm$^3$. The eluent was collected weekly and analysed for both $NO_3^-$ and $NH_4^+$ concentrations using FIA. Columns were leached under laboratory conditions (20$^o$C) for at least three months, or until the $NH_4^+$ and $NO_3^-$ concentrations in the eluent had stabilized at levels ≤ 5% of the concentrations recorded in the initial flush.

## 6.4 Lysimeter field experiment

### 6.4.1 Lysimeter setup

Eighteen undisturbed soil monolith lysimeters 0.5 m in diameter, and 0.7 m deep, containing Lismore stony soil, were taken from the Ashley Dene sheep farm Canterbury, New Zealand (43$^o$39′05.82″S 172$^o$19′41.47″E). The lysimeters were installed at the Lincoln University Field Service Centre (Figure 6-1). The design of lysimeter castings and method of sampling is described in detail by Cameron et al. (1992).

There were six treatments, each replicated three times. Biosolids, NV lignite and urea were applied separately at rates of 400 kg N/ ha, 20 t/ ha and 200 kg N/ ha respectively. A further three treatments consisted of either biosolids+lignite, urea+lignite and a control with no addition applied.

The application of each treatment occurred on the 16$^{th}$ of May 2012. To stimulate biosolids amendment to soil, the top 10 cm of soil in each lysimeter was removed and mixed with the applicable treatment in a concrete mixer for one minute. The control lysimeters were treated in an identical manner. Following treatment applications 0.5 g of tetraploid perennial ryegrass (*Lolium perenne* L. var Bronsyn) was broadcast by hand over each lysimeter. Ten litre containers were installed at the base of the lysimeters for leachate collection. (***NOTE****: See* Appendix B *for more photographs of instillation of lysimeter and treatment addition).*

Figure 6-1. *Left*: Installation of lysimeters; *Right*: Gas chambers just before the gas collection.

Table 6.2. Chemical properties of the pasture grown on the lysimeters. Values represent the mean (n=3). Values in brackets are the standard error of the mean. Values with the same letter are not significantly different at the 5% level (ANOVA with Fisher's test).

| | **Soil Treatments** | | | | | |
|---|---|---|---|---|---|---|
| | **Control** | **Lignite** | **Biosolids** | **Biosolids + Lignite** | **Urea** | **Urea + Lignite** |
| Total C (g/kg) | 439 (2.5)$^{ab}$ | 441 (2.3)$^{ab}$ | 442 (2.1)$^{a}$ | 443 (0.8)$^{a}$ | 441 (1.3)$^{ab}$ | 434 (3.7)$^{b}$ |
| Total N (g/kg) | 25.3 (0.8)$^{a}$ | 24.2 (0.6)$^{a}$ | 25.3 (1.6)$^{a}$ | 25 (2.1)$^{a}$ | 24 (1.6)$^{a}$ | 23.8 (0.3)$^{a}$ |
| P (mg/kg) | 4511 (145)$^{ab}$ | 4585 (93)$^{ab}$ | 4084 (124)$^{b}$ | 4121 (121)$^{b}$ | 4421 (237.3)$^{ab}$ | 4738 (265)$^{a}$ |
| S (mg/kg) | 2292 (119)$^{a}$ | 2714 (74)$^{a}$ | 2469 (228)$^{a}$ | 2408 (226)$^{a}$ | 2729 (270.5)$^{a}$ | 2826(78)$^{a}$ |
| Ca (mg/kg) | 7898 (569)$^{a}$ | 6888 (150)$^{b}$ | 7920 (309)$^{a}$ | 7502 (331)$^{ab}$ | 7917 (147)$^{a}$ | 8270 (220)$^{a}$ |
| Mg (mg/kg) | 914 (18.8)$^{bc}$ | 983 (40.9)$^{ab}$ | 840 (53.8)$^{c}$ | 918 (20)$^{b}$ | 921 (82.4)$^{bc}$ | 1073 (26.3)$^{a}$ |
| K (mg/kg) | 24170 (967)$^{ab}$ | 23888 (389)$^{ab}$ | 21055 (982)$^{c}$ | 21158 (319)$^{c}$ | 21609 (780)$^{bc}$ | 25274 (1244)$^{a}$ |
| Na (mg/kg) | 1461 (40)$^{a}$ | 1464 (114)$^{a}$ | 1887 (274)$^{a}$ | 1925 (352)$^{a}$ | 1819 (176)$^{a}$ | 1304(75)$^{a}$ |
| Al (mg/kg) | 429 (107)$^{ab}$ | 422 (45)$^{ab}$ | 279 (35)$^{b}$ | 400 (54.7)$^{ab}$ | 357 (26.7)$^{ab}$ | 519 (89.8)$^{a}$ |
| Cu (mg/kg) | 4.4 (0.3)$^{b}$ | 4.5 (0.3)$^{b}$ | 6.2 (0.4)$^{a}$ | 5.3 (0.4)$^{ab}$ | 5.2 (0.4)$^{ab}$ | 5.1 (0.2)$^{b}$ |
| Cd (mg/kg) | 0.07 (0.05)$^{a}$ | 0.01 (0.0)$^{a}$ | 0.02 (0.01)$^{a}$ | 0.02 (0.0)$^{a}$ | 0.02 (0.0)$^{a}$ | 0.02 (0.0)$^{a}$ |
| Fe (mg/kg) | 327 (68)$^{ab}$ | 324 (35)$^{ab}$ | 231 (28)$^{b}$ | 306 (35.9)$^{ab}$ | 295 (12)$^{ab}$ | 392 (70)$^{a}$ |
| Mn (mg/kg) | 20.7 (2)$^{c}$ | 33.9 (5.6)$^{c}$ | 23.4 (3.6)$^{c}$ | 24.1 (1.3)$^{c}$ | 76 (11.2)$^{b}$ | 102 (12.3)$^{a}$ |
| Zn (mg/kg) | 15.4 (0.7)$^{b}$ | 14.8 (0.2)$^{b}$ | 21.9 (2)$^{a}$ | 20.0 (1)$^{a}$ | 15.1 (0.5)$^{b}$ | 16.3 (1)$^{b}$ |

## 6.5 Sample Collection

### 6.5.1 Leachate

Lysimeter drainage was collected bi-weekly or more frequently following heavy rain. The volume of drainage was measured and a 70 mL subsample taken and stored immediately in a freezer for subsequent analysis of both $NO_3^-$ and $NH_4^+$ using FIA.

### 6.5.2 Herbage

Herbage was harvested on three occasions (28$^{th}$ of Sep 2012, 16$^{th}$ of Jan 2013 and 15$^{th}$ of Mar 2013) when pasture reached typical pre-grazing levels of dry mater (DM). Hand shears were used to clip the pasture to a height of 2 cm.

## 6.6 Climate and irrigation

Simulated rainfall was applied (if required) to all lysimeters to supplement a shortage of natural rainfall with the aim of meeting the 75$^{th}$ percentile of rainfall based on a 25 years rainfall record.

## 6.7 Gas sampling- collection and analysis

### 6.7.1 Soil moisture and temperature

The average soil water content in the lysimeter (0-15 cm depth) was measured using a Hydrosense moisture probe (15 cm) (Campbell Scientific, Utah, USA). Soil temperature was recorded using a 107-L temperature sensor (Campbell Scientific, Utah, USA) to measure the soil temperature at 7.5 cm depth. A data logger (CR23X, Campbell Scientific, Utah, USA) was used to collect soil moisture and temperature information every ten minutes during the $N_2O$ measurement periods, while hourly and daily averages were also recorded throughout the experiment. Both moisture and temperature probes were installed prior to $N_2O$ gas sample collection.

### 6.7.2 Nitrous oxide gas collection

A standard closed chamber method (Figure 6-1) similar to that described by Hutchinson and Mosier (1981) was used to determine $N_2O$ emissions from the lysimeters. Sampling was carried out over a four week period starting 7$^{th}$ May 2013, in which samples were collected every day for seven days and every second or third day for the remaining weeks. An initial gas sample was taken prior to treatment application. Gas samples were collected between 12.30 pm and 2.30 pm. The gas chamber was constructed from a metal cylinder, insulated on the outside with 2.5 mm thick polystyrene foam to avoid heating of the chamber head space during sampling. An annular ring mounted on the monolith lysimeters formed a U-shaped water trough around the lysimeter to which the chamber was fitted during sampling to create an air-tight seal. A rubber septum in the chamber surface facilitated gas sampling. At each sampling time, the chamber was placed on top of the lysimeter for a total of 60 minutes, and three samples (25 mL), were collected. Samples were collected in 6 mL Exetainer® vials which had been pre-evacuated (-1 atm) according to de Klein et al. (2001). The air temperature was recorded prior to sampling followed by measurements of the chamber air temperature at 20, 40 and 60 minutes.

Nitrous oxide concentrations were determined at New Zealand's National Centre for Nitrous Oxide Measurement (NZ-NCNM) at Lincoln University, New Zealand using a gas chromatograph (GC) (SRI 8610 gas chromatograph; SRI Instruments, CA, USA) fitted with a $^{63}$Ni electron capture detector (ECD), and linked to an autosampler (Gilson 222 XL; Gilson Inc., WI, USA). PeakSimple software (SRI Instruments, CA, USA) was used to control and monitor the ECD. The $N_2O$ fluxes (g $N_2O$-N ha/d) were calculated using the change in headspace $N_2O$ concentration (μL/L) over time and the protocols and equations of Hutchinson and Mosier (1981). A full description of the GC and its operation can be found elsewhere (Kelliher et al., 2012).

Data were analysed using Minitab® 16 (Minitab Inc, State College, Pennsylvania, USA). Data sets were analysed using ANOVA with Fisher's Least-Significant-Difference post-hoc test to compare means. The level of significance was 0.05.

## 6.8 Results and discussion

Batch sorption experiments revealed there was negligible $NH_4^+$ sorption by the Lismore soil and the Charleston and Millerton lignites. In contrast, there was significant $NH_4^+$ sorption by the NV lignite. Figure 6-2 shows the $NH_4^+$ sorption by the NV lignite at solution pHs between 4.1 and 6.7. Ammonium sorption by the NV lignite increased with increasing pH. This is consistent with there being a pH dependent variable charge on the NV lignite.

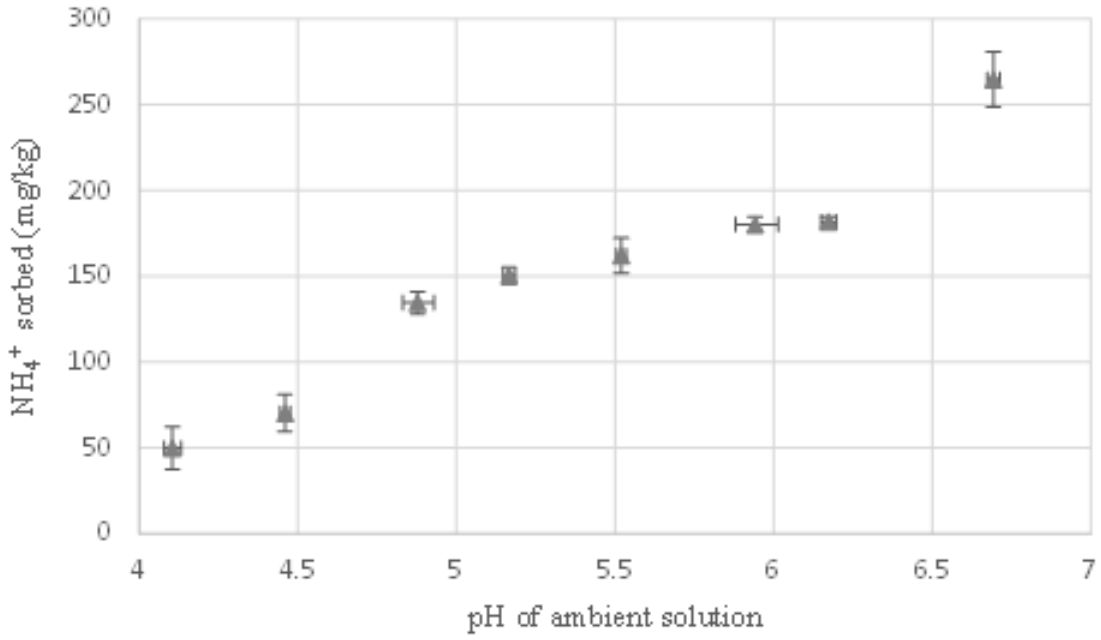


Figure 6-2. $NH_4^+$ sorbed (mg/kg) by the NV lignite from a 100 mg/L $NH_4^+$ solution at various solution pH values. Material: solution ratio 1:10. Bars represent the standard error of the mean (n=3).

Nitrate sorption on the lignite did not occur during the batch sorption and this is consistent with the negative surface charge on the NV lignite (Simmler et al., 2013). Lignite

materials have been adopted to adsorb $NO_3^-$ by modifying the surface using chemical ($ZnCl_2$) and thermal activation (Khan et al., 2011). Given that most mineral-N in aged biosolids is in the form of $NO_3^-$ (Bernal et al., 1998; Smith et al., 1998), it is unlikely that lignite would prevent the initial flush of N leaching from biosolids-amended soil. The results of the column leaching study agree with this supposition, with the addition of increasing rates of NV lignite making no difference to the amount of $NO_3^-$ leached (Figure 6-3) and where the amount of $NO_3^-$-N lost was ca 5-fold greater than the highest $NH_4^+$ loss.

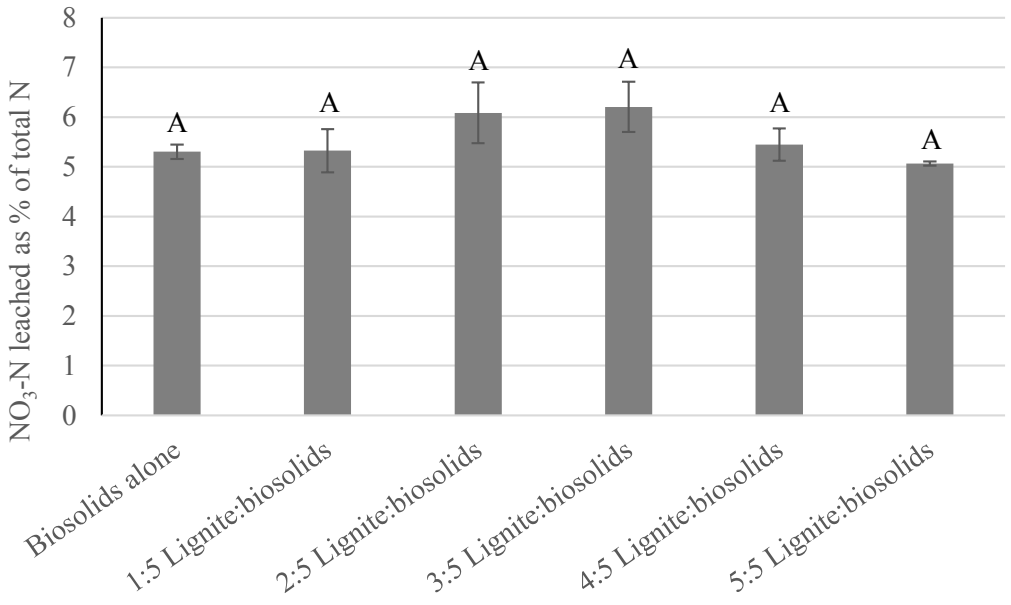


Figure 6-3. $NO_3^-$-N leached, as a percentage of N applied, from columns with NV lignite mixed with biosolids. Number ratios indicate the mass of lignite (g): mass of biosolids (g). Bars represent the standard error of the mean (n=3). Bars with the same letter are not significantly different at the 5% level (ANOVA with Fisher's test).

In contrast, younger biosolids, which have a significant $NH_4^+$ component of their mineral N, may leach less N if amended with lignite to retain $NH_4^+$ Increasing the amount of NV lignite added to the biosolids significantly reduced the mass of $NH_4^+$-N that leached from the columns (Figure 6-4). However, above a NV lignite: biosolids ratio of 2:5, there was no further decrease in $NH_4^+$-N leaching.

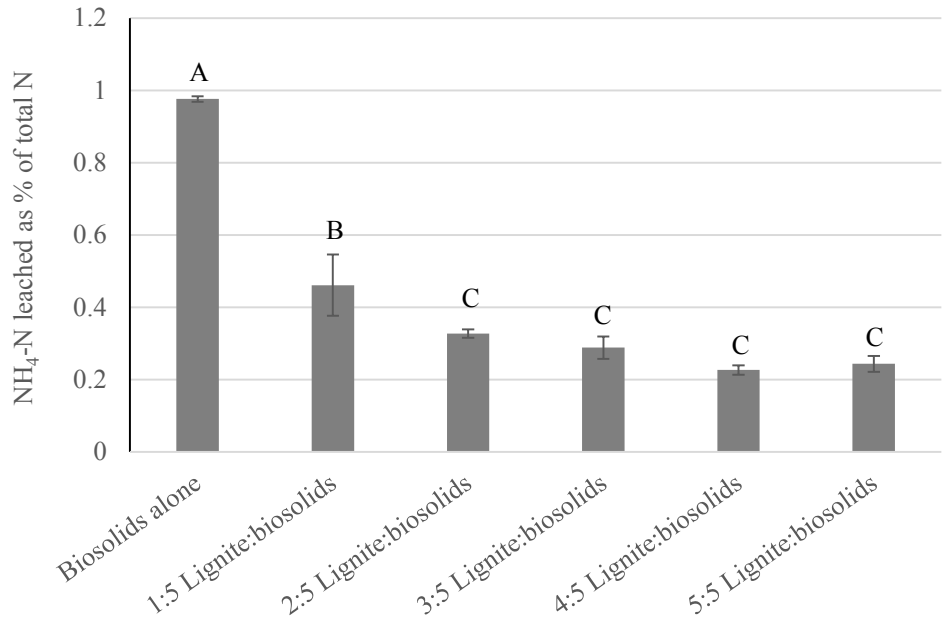


Figure 6-4. $NH_4^+$-N leached, as a percentage of N applied, from columns with NV lignite mixed with biosolids. Number ratios indicate the mass of lignite (g): mass of biosolids (g). Bars represent the standard error of the mean (n=3). Bars with the same letter are not significantly different at the 5% level (ANOVA with Fisher's test).

The total cation exchange sites in the columns equated to $2.0\times10^{-3}$ mol of negatively charged sites and this was significantly higher than the total potential $NH_4^+$-N available (assuming complete mineralization of both NV lignite and biosolids) of $1.1\times10^{-5}$ mol. However, $NH_4^+$ ions compete with other cations $Al^{3+}$, $Ca^{2+}$, $K^+$ and $Na^+$ for these sites. The positive charge from these ions in our columns was >0.006 mol, in excess of the total moles of negative charged surface.

A second mechanism for the reduction in $NH_4^+$-N leaching with an increasing NV lignite rate could be the microbial immobilization of $NH_4^+$, due to the increasing availability of water WSC as lignite rates increase (Ghani et al., 2003).

Between April and November, the lysimeters received 1105 mm of rainfall + irrigation, equating to 221 L per lysimeter. The monthly average air temperature in April was 12ºC,

decreased to 5.5 - 6.5°C in June - July, before increasing in spring to 10 - 11°C in October-November. The total N leached as $NH_4^+$-N from the lysimeters varied between 6.7 - 10 mg which is equivalent to 0.33 and 0.50 kg/ha (data not shown) and was insignificant compared to the $NO_3^-$-N leached (524 - 3207 mg, equivalent to 26 kg/ha – 160 kg/ha). The high CEC of the NV lignite (Table 6.1) indicates that adding the NV lignite to the Lismore soil will increase the total CEC. This increase in CEC may be offset by the acidic pH of the NV (Table 6.1) compared to the Lismore soil (6.3). The contrasting effects of increased CEC and reduced pH caused by lignite addition have been highlighted by Pehlivan and Arslan (2006) and Simmler et al. (2013).

Sorption of $NH_4^+$ by the lignite may result in prolonged retention of N in the plant root-zone allowing greater plant uptake, and reducing N-leaching. Richards et al. (1986) showed that lignite significantly increased the growth of tomato and two ornamental plants which they attributed to the high CEC of the lignite (ca. 60 $cmol_c/kg$).

Figure 6-5 shows the $NO_3^-$-N leached as a percentage of the total N (soil N and amendments) in the top 10 cm of soil, i.e. the soil into which the treatments were mixed. The lignite-only treatment leached less $NO_3^-$-N compared to the control ($p< 0.05$). However, in the biosolids and urea treatments, the addition of lignite had no significant effect on the amount of N leached. The lack of any effect of lignite on N-leaching from the biosolids can be explained if most of the mineral N in the biosolids was present as $NO_3^-$, which the batch sorption and column leaching experiments demonstrated was not sorbed by the lignite. However, the lack of any effect of lignite on $NO_3^-$-N leaching from the urea treatment was unexpected, since urea hydrolyses to form $NH_4^+$ and it was expected that this would be partially retained by the lignite. Since the addition of lignite increased CEC by 5.56% potentially alter the retention of all urea-N as $NH_4^+$ on the increased CEC.

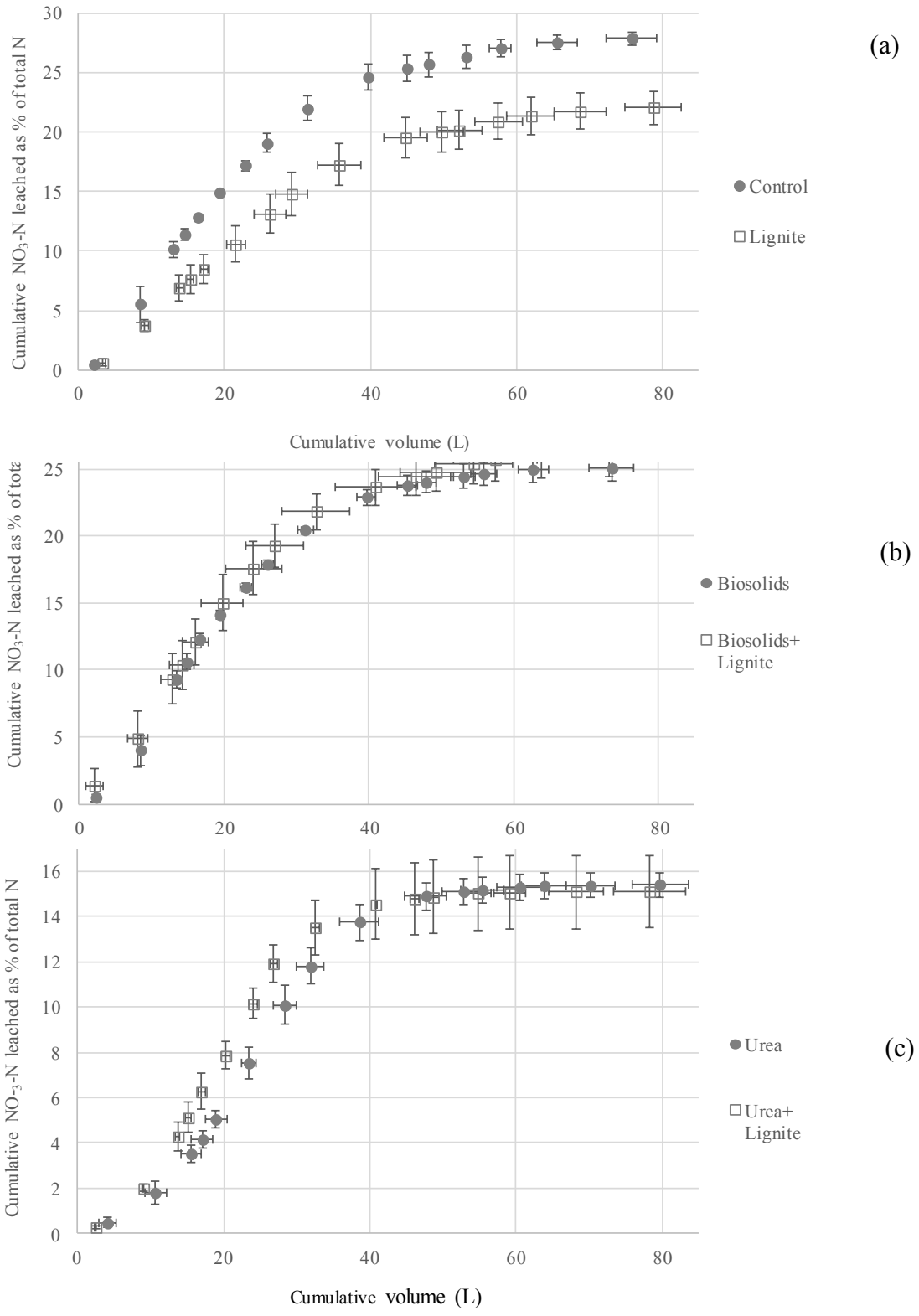


Figure 6-5. Cumulative $NO_3^-$-N leached as percentage of total N applied in each lysimeters. (a) comparison of lignite treatment with control lysimeters, (b) biosolids treatment with biosolids+ lignite treatment lysimeters, (c) urea treatment with urea +lignite treatment lysimeters.

The lysimeter experiment was conducted from autumn to spring, which is when most leaching from pasture occurs (Di & Cameron, 2007) and when pasture growth is low relative to the summer months. The lysimeters produced between 1000 to 2500 kg DM/ha. *Lolium perenne* L. is reported to produce 14200-23400 kg DM/ha/year (Glassey et al., 2010) with most of this growth occurring in the warmer months. The pasture in our experiments removed the equivalent of 25 – 62.5 kg N/ha, less than the amount of N added (200 – 400 kg N/ha equivalent). Therefore, it is unlikely the pasture would have been unable to remove any additional $NH_4^+$ that was detained in the root-zone by the lignite.

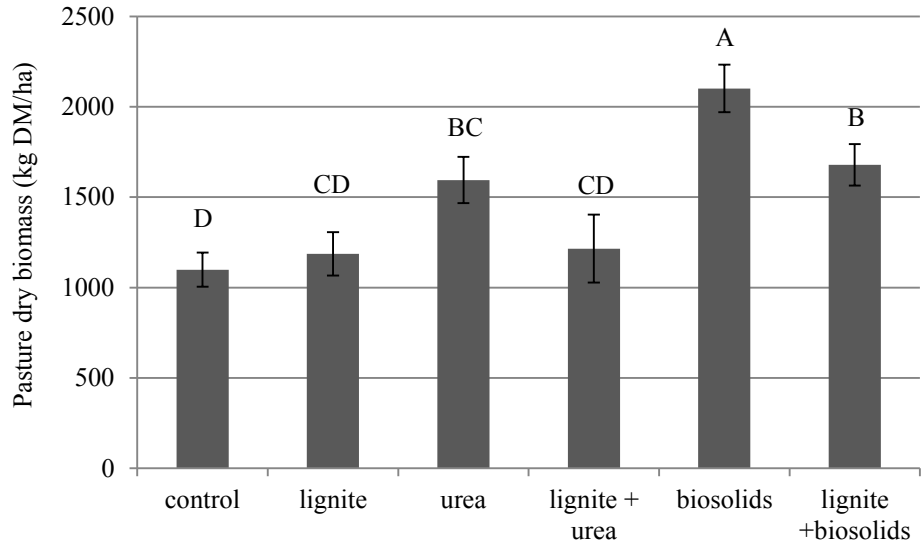


Figure 6-6. Total biomass (DM) of pasture harvested from each lysimeter, calculated per hectare. Bars represent the standard error of the mean (n=3). Bars with the same letter are not significantly different at the 5% level (ANOVA with Fisher's test).

The lignite was incorporated into the top 10 cm of soil in order to try and modify urea-N cycling. In contrast, previous studies have used "black urea", which is a mixture of urea and lignite. Thus, current results do not necessarily indicate that adding lignite to urea as "black urea" would be ineffective in reducing $NO_3^-$-N leaching. However, the results do indicate that the addition of lignite to soil is unlikely to reduce N leaching from surface-applied urea.

The growth of pasture increased following the addition of urea, biosolids and biosolids + lignite ($p < 0.05$). Adding lignite to the biosolids, however, reduced the pasture yield (Figure 6-6) compared to biosolids alone, whereas adding lignite + urea did not significantly reduce yield compared to urea alone. In the control soil, the addition of lignite had no effect on pasture yield. The treatments had only a minor effect on the elemental composition of the pasture (Table 6.2) with the addition of biosolids significantly increasing the pasture Zn concentration, while lignite addition did not reduce heavy metal concentrations in any treatment.

There were no detectable $N_2O$ emissions (< 2.5 g $N_2O$-N/ha) from the control or lignite treatments over the 28 d period (Figure 6-7a). The addition of biosolids alone did not significantly increase $N_2O$ emissions over the entire experimental period (Figure 6-8). Figure 6-7b shows that during the experimental period, the biosolids + lignite treatment emitted significantly more $N_2O$ than the biosolids alone treatment on day 3 and visa-versa on day 10. The addition of urea increased daily and cumulative $N_2O$ emissions (Figure 6-8) and this increase was exacerbated by lignite (Figure 6-7c, Figure 6-8). This may have been a consequence of the increased availability of lignite derived WSC enhancing denitrification, since WSC has been shown to correspond to denitrification rates (Burford & Bremner, 1975), or lignite addition may have altered (Table 6.1) soil physical properties which may have resulted in higher $N_2O$ emissions (Schmidt et al., 1999). Alternatively, lignite addition may have increased the nitrification rate of urea N, thereby increasing the supply of source $NO_3^-$ for subsequent denitrification. In contrast, the N-available for nitrification in biosolids is low compared to urea.

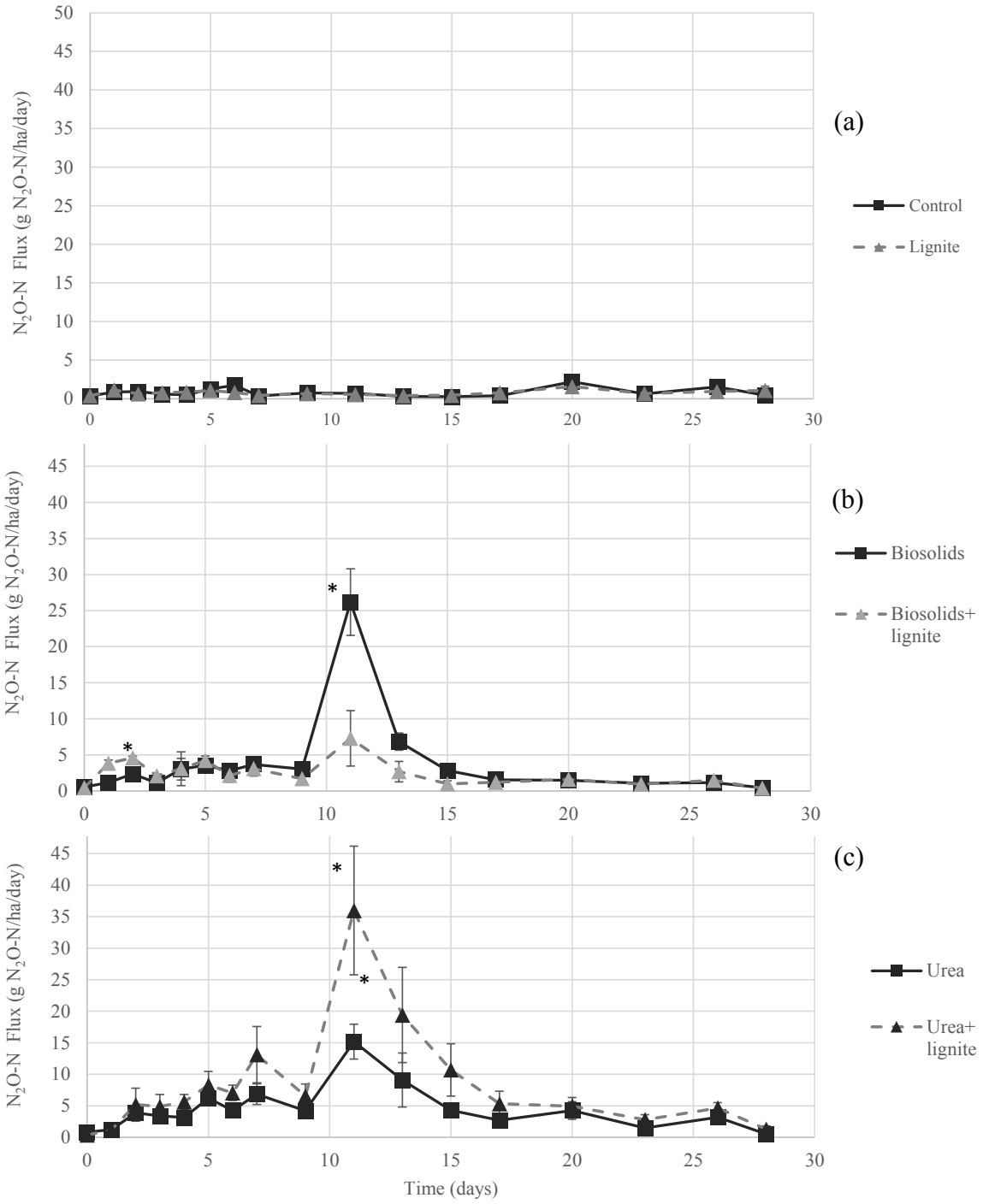


Figure 6-7. Daily $N_2O$ fluxes (g $N_2O$-N ha/day) over time showing (a) flux between control and lignite treatments (b) biosolids and biosolids + lignite and (c) urea and urea + lignite treatments over a 28 day period. Error bars are standard error of the mean (n = 3). Asterisks denote significant differences ($p<0.05$).

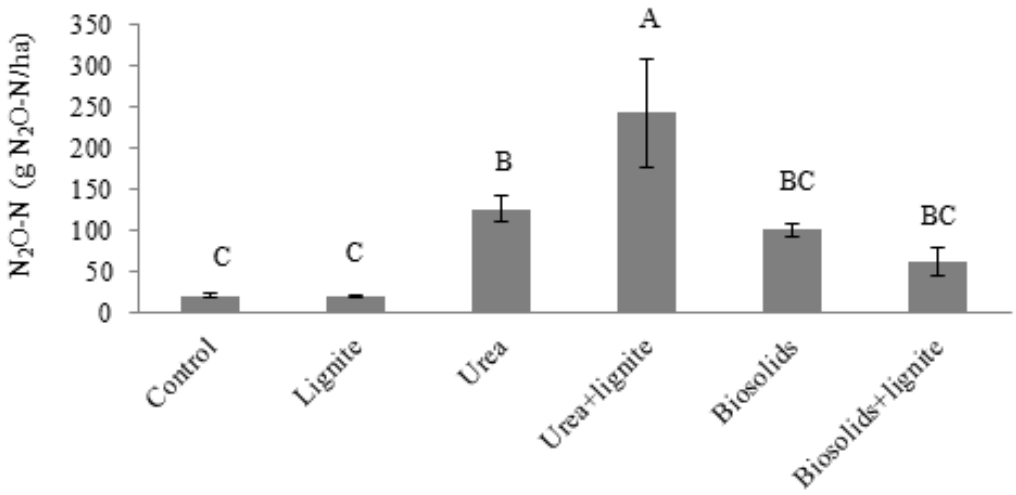


Figure 6-8. Average cumulative $N_2O$ loss (g $N_2O$-N/ha/day) over 28 days. Error bars are standard error of the mean (n = 3). Values with the same letter are not significantly different at the 5% level (ANOVA with Fisher's test).

## 6.9 Conclusions

The addition of lignite to soil did not significantly offset the increase in $NO_3^-$ leaching caused by adding biosolids or urea. There was a small reduction in $NO_3^-$ leaching from unamended soil, which corresponded to the increase in cation exchange sites by 3.33 mol in a lysimeter. This reduction is unlikely to be significant in an agricultural context. Lignite exacerbated $N_2O$ emissions from soils receiving urea. Furthermore, lignite lessened the beneficial growth effects of adding biosolids or urea to soil. Future work should investigate whether coating urea granules with lignite results in lower reactive N losses from pastures.

# Chapter 7: Effect of carbonaceous materials on rye grass biomass yield and N uptake in soils treated with biosolids.

This work was performed *inter alia* with the MSc experiments of Michael Simmler (Simmler et al., 2013) and Jörg Gartler (Gartler et al., 2013), as well as studies conducted by Dr Juergen Esperschuetz (under review) who studied the effect of these amendments on metal uptake.

## 7.1 Abstract

Previous work has demonstrated the effects of biosolids-sawdust mixtures on plant growth; however, there is a lack of information on the effects of biosolids/biochar or biosolids/lignite mixtures on plant growth. Experiments investigating the effects of biowaste mixtures on metal uptake were performed *inter alia* with the aim of determining how combining biowastes with carbonaceous materials would affect the growth and nitrogen (N) uptake of perennial ryegrass (*Lolium perenne* L.). This chapter presents the results of three independent pot trials.

Under greenhouse conditions, ryegrass (*Lolium perenne* L.) was grown with biosolids alone or with biosolids mixed with either sawdust, biochar or lignite up to 1:1 ratios (similar to those used in Chapters 5 & 6). When sawdust was combined with biosolids, plant biomass was reduced by ca. 25% compared to biosolids alone. Mixing biosolids with biochar increased biomass by up to 20%. Lignite combined with biosolids increased biomass by 44%. There was no consistent effect on plant N uptake when biosolids were mixed with either sawdust, biochar or lignite.

## 7.2 Introduction

The work presented in Chapters 5 and 6 showed that sawdust, biochar or lignite could all reduce the mobility of N released from biosolids. It is therefore likely that mixing these waste materials with biosolids may enable biosolids to be applied at rates required to rebuild

degraded soils, without an increase in N leaching. Such mixtures would not only add organic matter and plant nutrients to soil, but also reduce the burden on landfills and reduce costs involved with the disposal of these waste materials. Research examining crop growth under biosolids and carbonaceous materials such as biochar, has produced mixed results. For example, both materials have been shown to increase the biomass of beet root (*Beta vulgaris*), radish (*Raphanus sativus*), onion (*Allium cepa*) and decrease biomass of some leafy vegetables e.g. spinach (*Spinacia oleracea*), lettuce (*Lactuca sativa*) (Gartler et al., 2013). Knowles et al. (2011) showed that biochar incorporated with biosolids decreased ryegrass biomass when compared to biosolids alone. However, they did not include a biochar treatment to determine whether biochar had a toxic effect or if it affected the growth by sorbed nutrient (which might not be plant-available) from the amended soil. Reduction in available N and other nutrients, were not investigated by these authors (Knowles et al., 2011). Chapter 6 demonstrated that the benefits of adding biosolids, in terms of ryegrass growth, were significantly offset by added lignite. Nevertheless, ryegrass growth on soils amended with both biosolids and lignite was significantly higher than the control. A similar outcome was showed by Simmler et al. (2013)

Previous studies have shown that sawdust applied to soil can reduce plant growth (Barney & Colt, 1991; Trolove & Reid, 2003; Trolove et al., 2005) due to the immobilization of N and other plant nutrients. Barney and Colt (1991) showed sawdust could be used as a growth medium for plants provided three issues were addressed:

(1) N and other plant nutrient depletion,
(2) soil acidification and
(3) toxicity of certain woody materials.

Barney and Colt (1991) demonstrated that (1) a mixture of hardwood and softwood mulch can be made fertile by incorporation of 10 kg N/t and 6 kg N/t respectively, (2) incorporation of these wood products into soil causes negligible change in pH, and (3) the leachate from some woody materials can be toxic to fresh water fish. Therefore, leachate must

be prevented from entering surface water. If leachate reacts with metals in the soil, it will rapidly loses its toxic and corrosive character (Barney & Colt, 1991). Wood-waste is a possible soil amendment when addressing the issues mentioned above.

There is, however, considerable variation in plant growth and soil responses to biochar. Biederman and Harpole (2013) state that the effect of biochar on plant growth cannot be evaluated in a single study. Feedstock material and pyrolysis conditions introduce significant variation in the structure, nutrient content, pH, and phenolic/PAHs content of the biochar products (Novak et al., 2009). In addition to these, growth can also be affected by soil type and climate. Kammann et al. (2015) showed that in temperate soils, pure biochar (uncomposted) showed moderately negative to positive yield effects. The addition of 2% (w/w) uncomposted biochar decreased the biomass of *Chenopodium quinoa* (grain crop) by 60% compared to the control, while the composted biochar at the 2% (w/w) rate (input materials for the composting were animal manures, straw, rock powder, soil and mature compost) showed biomass yield increased up to 305% in a sandy-poor soil amendment. A similar observation was reported by Gundale and DeLuca (2007), with *Koeleria macrantha,* a perennial grass, where soil was amended with biochars produced at 350°C from ponderosa pine and Douglas fir bark. Both these biochars, added at a treatment rate of 2% w/w, reduced total biomass (by 36%) compared to the control (no char addition). In another pot experiment, these authors showed increased growth rates of the same grass with incorporation of char collected from a wildfire site (0.5, 1, 2, 5 and 10% w/w application). Biomass increased with increased char addition. The 2% w/w rate showed (for convenience, comparison is with the same rate) biomass increased by 120%.

Lignite may also positively influence plant growth (Pusz, 2007; Richards et al., 1986). Pusz (2007) showed growth increased with a combined 4 strains of grass mixtrue (40% perennial ryegrass (*Lolium perenne*), 35% red fescue (*Festuca rubrics*), 15% Italian ryegrass (*Lolium multiflorum*), and 10% meadow-grass (Poa pratensis). Richards et al. (1986) showed

increased growth of tomato and some ornamental indoor plants with incorporation of lignite. Humate substances are natural organic compounds that make up 50 to 90% of the organic matter of peat, lignites, and the non-living organic matter of soil and water ecosystems, therefore Trevisan et al. (2010) showed that humic acid had positive effects on plant physiology (Maize seedlings) by improving soil structure and fertility and by influencing nutrient uptake and root development. Humic acid enhances root develpoment which increases plant growth and biomass production.

It was hypothesised that, mixing sawdust, biochars or lignite with biosolids could reduce plant N availability. Therefore, it might offset the beneficial growth response from adding biosolids. Incorporation of these materials could also have growth benefits via liming effects, retention of plant available nutrients, and could act like a slow release fertilizer, where the beneficial effects of N are realized over a longer period.

## 7.3 Aims: Growth effects and N uptake by *Lolium perenne* with these amendments.

### 7.3.1 Methods

#### 7.3.1.1 Sawdust incorporation with biosolids

A pot trial was conducted in the Lincoln University greenhouse facility in 2014, where 10 L pots (13 kg soil/pot), were used to grow Italian ryegrass (*Lolium multiflorum* "Feast II tetraploid Italian ryegrass") and 2.0 g seeds/pot were used. Mottled Argillic Pallic soil (Silt loam soil (WRC, 2011) was collected from Wairarapa (40° 45' 56.63" S, 175° 54' 42.08" E). This is representative of many low fertility soils found in marginal lands in New Zealand (Table 7.1). The soil had been under Manuka and Kanuka vegetation and had not received fertilizer inputs.

Soil was amended with *Pinus radiata* (pine) sawdust and biosolids (KBS at a rate of 1250 kg N/ha) treatments. Either sawdust (1% w/w, dry basis) alone, KBS (2.3% w/w, dry

basis) alone, sawdust with biosolids and a control, receiving no sawdust/biosolids addition, comprised the treatments Treatment mixtures were added as top layers, ryegrass seeds were sown into the treatment mixture and pots were irrigated to field capacity. There were six replicates of each treatment. The experiment began in early spring, 16$^{th}$ of September 2013. Ryegrass was harvested thrice, (on the 16$^{th}$ and 30$^{th}$ of October, and 11$^{th}$ of November 2013), by cutting with scissors 2 cm above the soil surface. Biomass was weighed, dried at 70$^{o}$C for 48 hr, then reweighed to determine dry weight. Samples were ground (<2 mm) using a 10 yellow-line, IKA® to prepare them for N analysis. This was performed on an Elementar analysis (details in Chapter 4) to measure the total N. ***Note****: Treatment mixtures were not analysed, because treatments were only surface application (not blended with soil).*

Table 7.1. Basic soil analysis of the Wairarapa soil.

| Parameters | Wairarapa soil |
|---|---|
| pH ($H_2O$) | 6.1 |
| Total N (%) | 0.5 |
| Total C (%) | 6.5 |
| CEC ($cmol_c/kg$) | 21 |
| Base saturation (%) | 55 |
| Organic matter (%) | 11.2 |
| Bulk density ($g/cm^3$) | 1.3 |
| **Inorganic elemental analysis (mg/kg)** | |
| Al | n/a |
| B | 29 (0.3) |
| Cd | 0.05 (0.00) |
| Ca | 4100 (100) |
| Cu | 4.2 (0.0) |
| Fe | 15461 (108) |
| Mg | 2000 (10) |
| Mn | 134 (3) |
| P | 500 (10) |
| K | 1900 (40) |
| Na | n/a |
| S | 400 (20) |
| Zn | 29 (0.0) |

n/a: not analysed.

#### 7.3.1.2 Biochar incorporation with biosolids

The pot trial was conducted (Figure 7-1 ) in the Lincoln University greenhouse facility in 2010, where 2.5 L pots holding ca. 3 kg of soil, were used to grow ryegrass (~50 seeds/pot). The treatments included two soil types, Silt loam soil (denoted as Soil 1) and Balmoral soil (a type of light gravelly river-terrace soil and denoted as Soil 2). The screened Silt loam soil was purchased from Parkhouse Garden Supplies, New Zealand (43° 32' 42.65"S, 172° 34' 30.57"E). The Balmoral soil was sampled from the former Balmoral pine forest (42° 48' 45.19"S, 172° 37' 32.8"E), a degraded, acid silt loam type soil (WRC, 2011). Soil properties are shown in Table 7.2. Bulk biochar/biosolids treatments included either the “bulk biochar” (2 % w/w dry basis) alone, the “KSB” alone (2.5 % w/w dry basis) or biochar with biosolids (same 2:2.5 ratio) and a control receiving no biosolids/biochar addition. Treatments were mixed with soil and included three replicates of each treatment. Pots were irrigated manually to field capacity and no fertilizer application included. The greenhouse experiment was set up on the 18th January 2010. Ryegrass was harvested thrice, on the 15th of February, 9th of March and 22nd of

April. Biomass was determined fresh and after drying at 70°C for 48 hr. Dried samples were then ground (<2mm) using a grinder (A 10 yellow-line, IKA®). Total N and C was analysed on an Elementar analyzer. The pH, elemental N and C of the treatment mixtures are given in Table 7.3.

Table 7.2. Chemical analysis of the two soils used in the biochar treatment on ryegrass growth.

| **General parameters** | **[a]Silt loam soil (soil 1)** | **[b]Balmoral soil (soil 2)** |
|---|---|---|
| pH ($H_2O$) | 5.7 (0.08) | 4.2 (0.02) |
| Total C (%) | 3.3 (0.4) | 2.4 (0.2) |
| Total N (%) | 0.2 (0.01) | 0.16 (0.006) |
| **Inorganic elemental analysis (mg/kg)** | | |
| Al | 16000 (1000) | n/a |
| B | 12 (0.6) | n/a |
| Cd | 0.28 (0.01) | 0.30 (0.01) |
| Ca | 5889 (389) | 1842 (73.2) |
| Cu | 7.3 (0.1) | 4.4 (0.14) |
| Fe | 14000 (100) | 18648 (164) |
| Mg | 2579 (61) | 2496 (17.2) |
| Mn | 237 (4.9) | n/a |
| P | 596 (7.0) | 612 (82.1) |
| K | 2958 (411) | 3488 (337) |
| Na | 392 (31) | 207 (6.6) |
| S | 245 (5.9) | 234 (28.7) |
| Zn | 52 (1.4) | 53.2 (0.78) |

[a]Data source (Gartler et al., 2013) and [b]data source is the MSc thesis of Jörg Gartler (2010); n/a –not analysed.

Table 7.3. The pH, N and C of each treatments with appropriate soils at the initiation of the pot experiment.

| | **[a]Silt loam soil (Soil 1)** | | | **[b]Balmoral soil (Soil 2)** | | |
|---|---|---|---|---|---|---|
| | Biosolids | Biochar | Biosolids + biochar | Biosolids | Biochar | Biosolids + biochar |
| pH | 5.5 | 5.7 | 5.6 | 4.2 (0.04) | 4.4 (0.04) | 4.2 0.02) |
| N (%) | 0.3 (0.02) | 0.3 (0.001) | 0.4 (0.03) | 0.3 (0.01) | 0.2 (0.005) | 0.4 (0.01) |
| C (%) | 3.7 (0.1) | 5.0 (0.3) | 5.7 (0.5) | 3.9 (0.2) | 4.3 (0.3) | 7.8 (0.3) |

[a] Data source (Gartler et al., 2013) and [b] data source is the MSc thesis of Jörg Gartler (2010).

Figure 7-1. Greenhouse pot experiments incorporating biochar and biosolids.

#### 7.3.1.3 NV Lignite incorporation with biosolids

The pot experiment was conducted in a greenhouse at Lincoln University New Zealand, in 2011. Ryegrass was grown (~50 seeds/pot) in 2.5 L pots holding ca. 3 kg of soil. According to New Zealand soil classification (Hewitt, 2010; WRC, 2011), the soil used in the experiment was a typic immature pallic silt loam soil (43°38'11.35" S 172°26'17.00" E). Physical chemical properties of the soil are given in Table 7.4. The NV Lignite (for properties see Chapter 4) and biosolids (KBS) treatments included either the NV lignite at three rates (1, 3.4 and 7.1 % w/w, dry basis) alone and the biosolids (KBS) were added (3.7 % w/w) alone or NV lignite with biosolids combined at the same ratios, and control treatments received no biosolids/NV lignite. In addition to the treatments where the natural pH of the soil was 5.1, an identical set of treatments raised the pH to 7 (by adding 65 g of Ravensdown AgLime/pot), because this trial was designed for metal uptake by ryegrass. All treatments were prepared using a concrete mixer and replicated 5 times for each treatment. The pH, elemental N and C of the treatment mixtures are given in Table 7.5. The filled pots were placed in a randomised block design and allowed to stand for two weeks in order to equilibrate. *L. perenne* was sown directly onto the wet soil

surface and a dense surface cover established in all pots. Pots were irrigated daily to its field capacity and no fertilizer was applied. The above ground biomass was harvested on the 2nd of November 2011, 29 days after sowing and the 2nd harvest on the 2nd of December 2011. Fresh weight, dried weight, grinding and analysis were as described above.

Table 7.4. Chemical analysis of the Pallic soil.

| **General parameters** | [a]Immature pallic soil |
|---|---|
| pH ($H_2O$) | 5.1 |
| CEC($cmol_c$/kg) | 12.3 |
| Base saturation (%) | 50.3 |
| Total C (%) | 3.3 (0.03) |
| Total N (%) | 0.3 (0.001) |
| **Inorganic elemental** analysis (mg/kg) | |
| B | 7.3 (1.0) |
| Cd | 0.13 (0.00) |
| Ca | 3229 (58) |
| Cu | 5 (0) |
| Fe | 17727 (353) |
| Mg | 3426 (71) |
| Mn | 357 (20) |
| Mo | 0.1 (0.01) |
| P | 732 (11) |
| K | 2541 (279) |
| S | 383 (6) |
| Zn | 70 (2) |

[a] Data source (Simmler et al., 2013).

Table 7.5. The pH, N and C of each treatments with appropriate soils at the initiation of the pot experiment.

| | | **Soil at pH 5** | | | | | |
|---|---|---|---|---|---|---|---|
| | **Biosolids** | **Lignite (3 rates)** | | | **Lignite (3 rates) + biosolids** | | |
| | | 1% | 3.4% | 7.1% | 1% | 3.4% | 7.1% |
| pH | 4.9 | 5.0 | 5.0 | 4.9 | 4.9 | 4.9 | 4.9 |
| Total N (%) | 0.4 (0.04) | 0.4 (0.01) | 0.3 (0.05) | 0.5 (0.007) | 0.4 (0.02) | 0.4 (0.008) | 0.4 (0.04) |
| Total C (g/kg) | 4.3 (0.4) | 3.9 (0.08) | 5.2 (0.3) | 7.4 (0.5) | 4.4 (0.07) | 5.7 (0.2) | 8.8 (1.0) |
| **Soil at pH 7** | | | | | | | |
| pH | 5.5 | 5.8 | 5.4 | 5.3 | 5.7 | 5.4 | 5.3 |

NB: Total N and C from the pH 7 were not analysed.

## 7.3.2 Results and discussion

### 7.3.2.1 Biomass and N uptake following sawdust incorporation

Biomass yields from all three harvests showed that fresh sawdust incorporated with biosolids reduced ryegrass growth when compared to biosolids alone (Figure 7-2). However, applying only biosolids increased ($p<0.05$) ryegrass growth as expected (because of its fertilizing properties). The detailed physical and chemical analyses of this sawdust were given in Chapter 4. Total biomass yield from all three harvests from the sawdust is given in Table 7.6

Table 7.6. Total biomass yield from the sawdust treatment

| Treatments | Total ryegrass dry biomass from all 3 harvests (g/pot) |
|---|---|
| Control soil | 6.1 (0.4)$^{c}$ |
| Biosolids alone | 11.3 (0.7)$^{a}$ |
| Sawdust + biosolids | 8.4 (0.5)$^{b}$ |

Superscript denotes the Fisher's method was used to analyse the statistical significance between the treatments

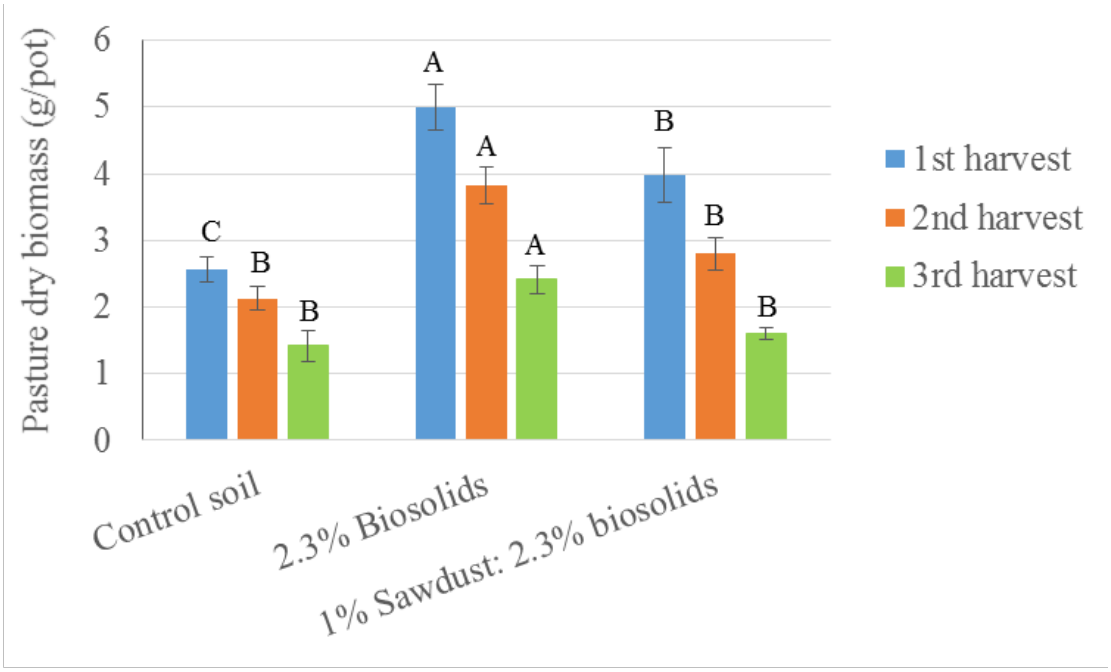


Figure 7-2. Ryegrass DM produced at three individual harvests in Wairarapa soil following incorporation of either biosolids or sawdust at the 1st harvest, 2nd harvest and 3rd harvest. Values are means (n=6) with error bar ± 5 standard error of the means. Letters are according to Fisher's method (confidence level 95%).

When considering the N uptake there were significant differences between treatments compared to control, mainly 1st and 3rd harvests (Figure 7-3). However, the 2nd harvest showed significantly higher N uptake by the biosolids alone but not with the combined biosolids +sawdust treatment (Figure 7-3).

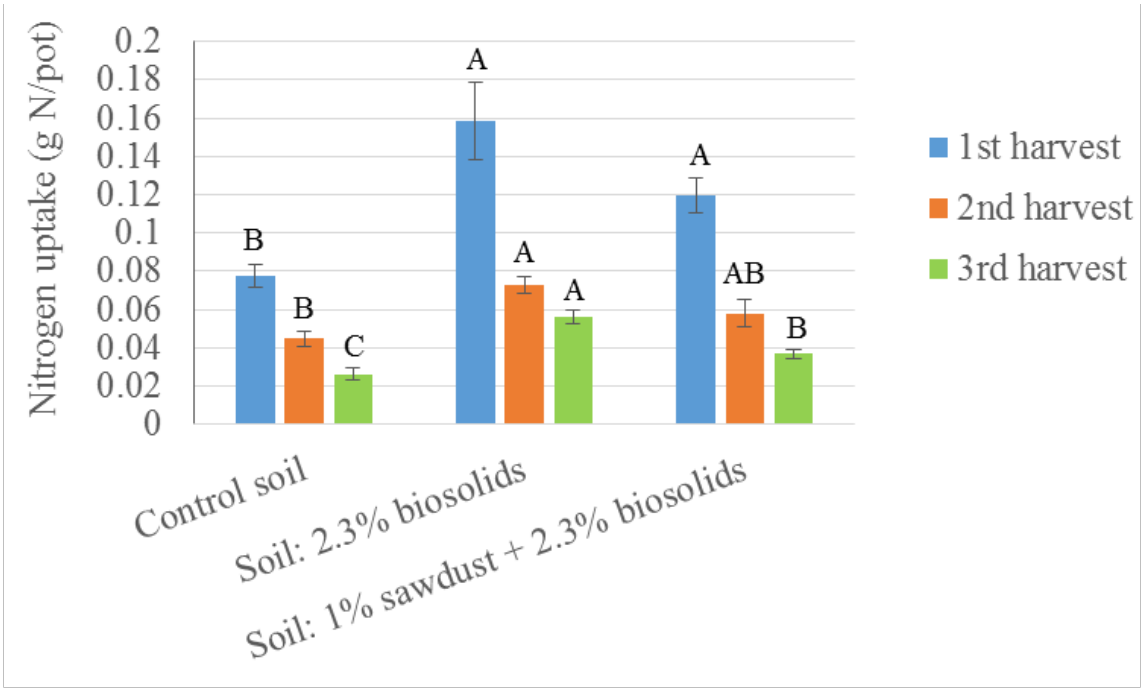


Figure 7-3. Nitrogen uptake at three individual harvests in Wairarapa soil following incorporation of either biosolids or sawdust combined with biosolids at the 1st harvest, 2nd harvest and 3rd harvest. Values are means (n=6) with error bar ± 5 standard error of the means. Letters are according to Fisher's method (confidence level 95%).

#### 7.3.2.2 Biomass and N uptake from the biochar incorporation

The physical chemical properties of Soils 1 and 2 are given in Table 7.2. Treatment mixtures in both soils and pH, total N and C are given in Table 7.3. The pH of the acidic Balmoral soil (Soil 2) rose from 4.2 (Table 7.3) to 4.4 due to the liming effect of biochar. Biochar alone had a pH of 6.9 (see

Table 4.5 in Chapter 4). The biosolids treatments did not alter the pH in Soil 2 and decreased the pH in Soil 1 (from pH 5.7 to 5.5). However, biochar and biosolids addition to these treatments increased both C and N overall (Table 7.3).

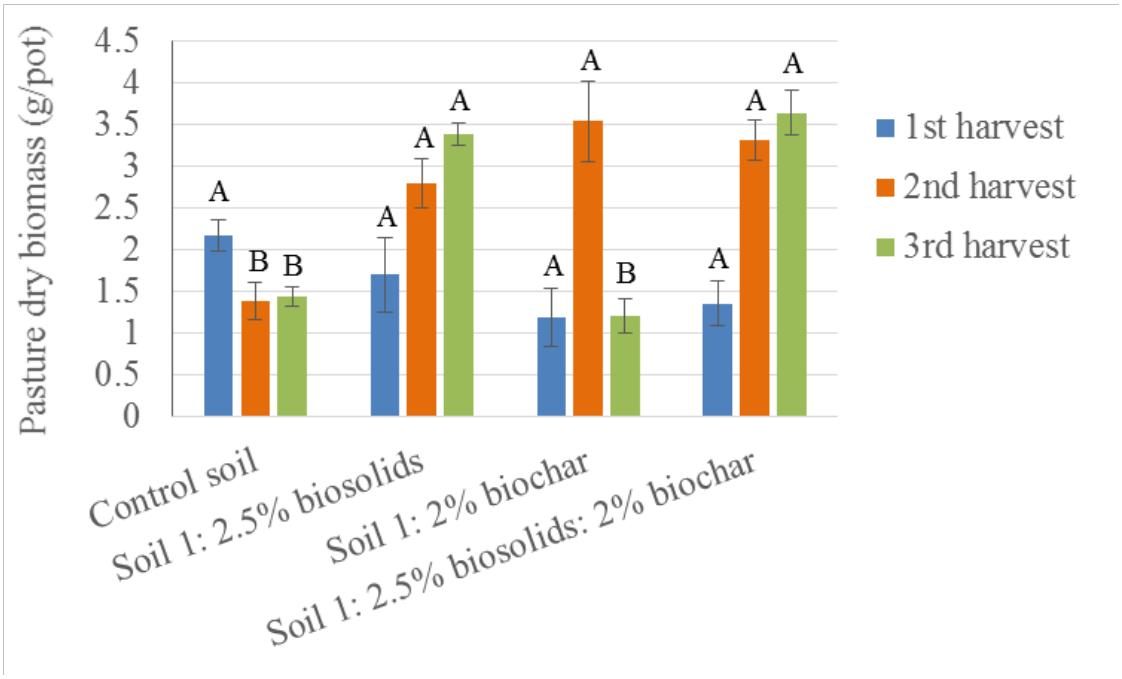


Figure 7-4. Ryegrass DM produced at three individual harvests in Silt loam soil (Soil 1) at the 1st harvest, 2nd harvest and 3rd harvest. Values are means (n=3) with error bar ± 5 standard error of the means. Letters are according to Fisher's method (confidence level 95%).

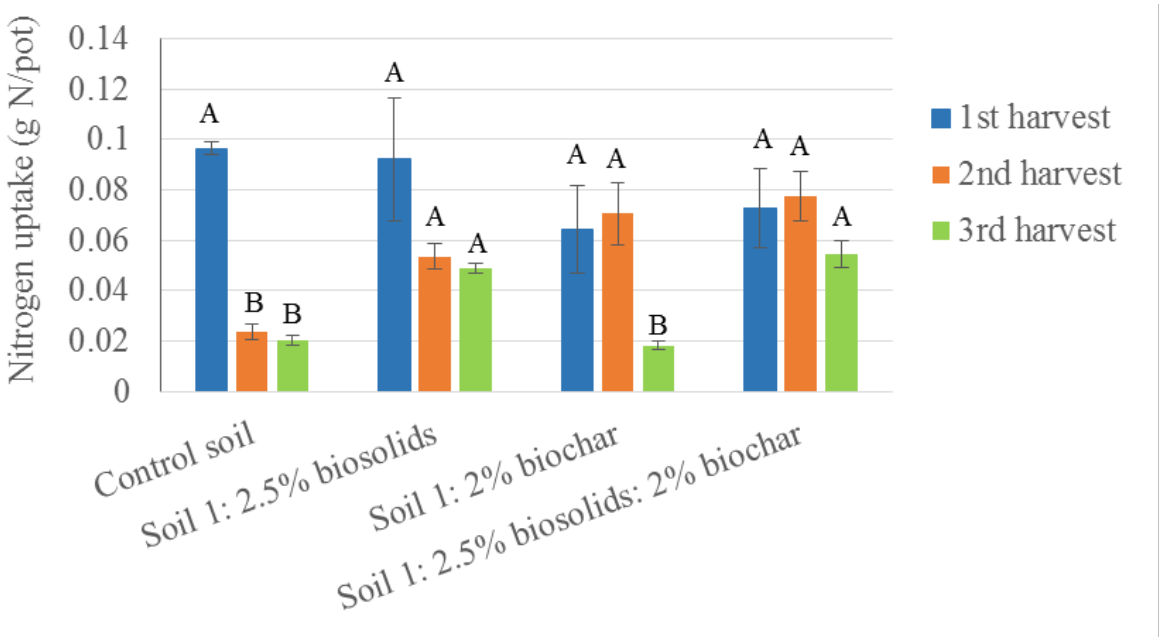


Figure 7-5. Nitrogen uptake at three individual harvests in Silt loam soil (Soil 1) following incorporation of either biosolids or sawdust combined with biosolids at the 1st harvest, 2nd harvest and 3rd harvest. Values are means (n=3) with error bar ± 5 standard error of the means. Letters are according to Fisher's method (confidence level 95%).

Figure 7-4 and Figure 7-5 show the ryegrass dry biomass and N uptake by the ryegrass over three harvests. The overall weight of biomass from the first harvest (highest yield was from the control 2.2g) was less, compared to the second (highest yield by biochar alone 3.5g) and last (highest yield by the combination of biochar and biosolids by 3.6g). Overall, treatments that included biosolids+biochar showed increased yield ($p<0.05$) except the first harvest. In the second harvest, all the treatments showed significantly higher biomass than the control, however, the third harvest showed a significant increase in biosolids, and biosolids+biochar treatments. Unexpectedly, the biochar alone treatment decreased plant growth significantly from the third harvest. Gundale and DeLuca (2007) showed that weathered biochar enhanced plant growth, compared to laboratory-produced charcoal. Their conclusion was that low-temperature charring method used to produce the charcoal in the laboratory might have created toxic compounds that inhibited plant growth. The total biomass yield from all three harvests from the biochar is shown in Table 7.7.

Table 7.7. Total biomass yield from biochar and biosolids treatment.

| | **Total ryegrass dry biomass from all 3 harvests (g/pot) soil 1** | **Total ryegrass dry biomass from all 3 harvests(g/pot) soil 2** |
|---|---|---|
| Control | 5 (0.1)$^{b}$ | 10 (0.9)$^{b}$ |
| Biosolids alone | 7.9 (0.7)$^{a}$ | 10.7 (0.7)$^{ab}$ |
| Biochar alone | 6 (0.3)$^{b}$ | 7.5 (0.2)$^{c}$ |
| Biochar+ biosolids | 8.3 (0.2)$^{a}$ | 12.5 (0.8)$^{a}$ |

Superscript alpha denotes the Fisher's significance method was used to analyse the statistical significance between the treatments.

N uptake showed significant increase in the 2$^{nd}$ and 3$^{rd}$ harvest, where the first harvest had no significant difference between treatments. Biochar alone treatment from the 2$^{nd}$ harvest showed an increase in N uptake. However, both 2$^{nd}$ and 3$^{rd}$ harvests of biochar+ biosolids treatment showed higher N uptake.

Figure 7-6 shows the ryegrass dry biomass and Figure 7-7 the N uptake for the Soil 2 treatments. The first two harvests showed significantly higher overall biomass (4.5 and 4.8 g)

in the biosolids+biochar treatment compared to the control. Unexpectedly, all three harvests showed a significant decrease in biomass yield in the biochar alone treatment compared to biosolids alone treatment, whereas Carter et al. (2013) found a significant increase of biomass yield of lettuce (903 %) and cabbage (750 %) in a soil amended with biochar at a rate of 50 g/kg (with no fertilizer addition).

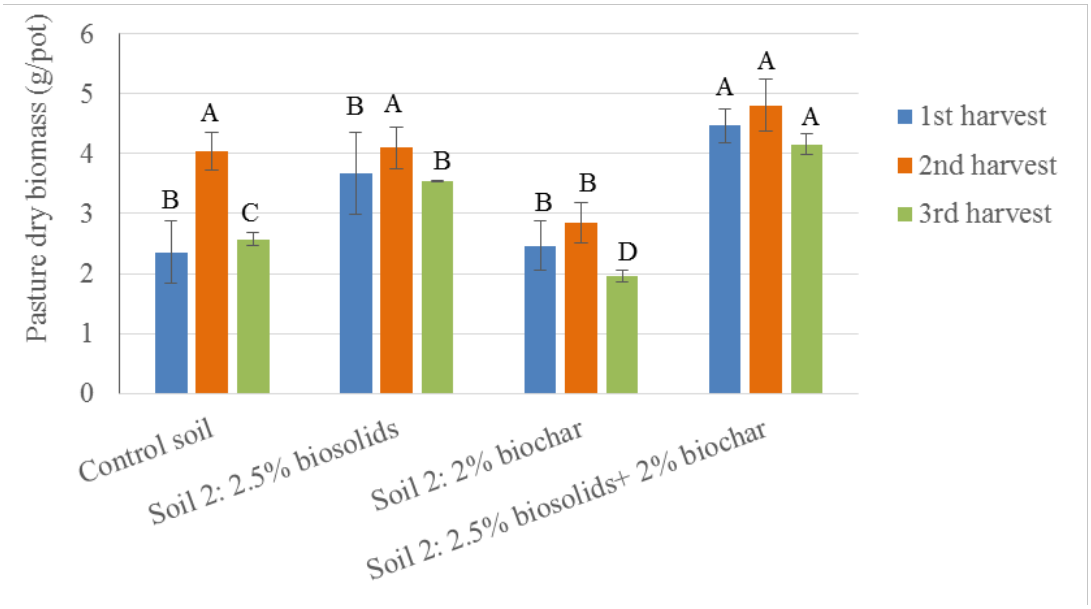


Figure 7-6. Ryegrass DM produced at three individual harvests in Balmoral soil (Soil 2) following incorporation of either biosolids or biochar at the 1st harvest, 2nd harvest and 3rd harvest. Values are means (n=3) with error bar ± 5 standard error of the means. Letters are according to Fisher's method (confidence level 95%).

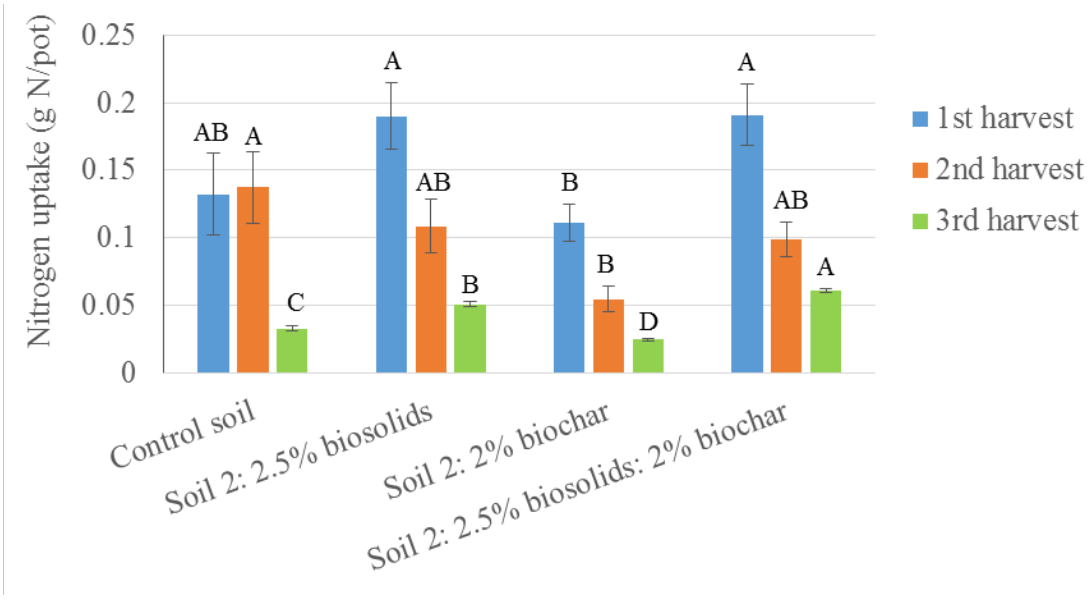


Figure 7-7. Nitrogen uptake at three individual harvests in Balmoral soil (Soil 2) at the 1st harvest, 2nd harvest and 3rd harvest. Mean dry biomass (n=3) of ryegrass amended with biowastes. Values are means

(n=3) with error bar ± 5 standard error of the means. Letters are according to Fisher's method (confidence level 95%).

Soil 2 was acidic (Table 7.1) compared to Soil 1, however, biochar incorporation slightly increased the pH of the growth soil mixture (Table 7.2). Considering the N uptake in Soil 2, there was variation between the treatments and among the harvests as well. Unexpectedly, N uptake between treatments was only significantly different in the 3$^{rd}$ harvest. All three harvests of biochar alone treatment showed a significant reduction in N uptake.

Soil pH is altered via biochar addition (also called "liming effect"), which is generally attributed to the alkalinity of ash content (Khanna et al., 1994). The liming effect of biochar could lead to an increase in plant growth (Biederman & Harpole, 2013). Another reason for biochar's influence in soil pH may be that the high surface area and the porous nature of biochar increases the CEC of the soil (Van Zwieten et al., 2010), however, this could decrease the pH eventually due to acidic functional groups.

Ruan et al. (2007) showed that the tea plant (*Camellia sinensis*) biomass yield and N uptake increased in soil pH around 5 regardless of applied N (authors did not use biosolids), and was decreased by a combination of high soil pH and $NO_3^-$. Toxic metals (e.g. $Al^{3+}$, $Cd^{2+}$) that exist in soil could be immobilized/removed (adsorbed) by the biochar liming effect, however, this was not shown with the biomass yield of Soil 2. This could be due to other factors, such as toxic poly-aromatic hydrocarbons (PAHs) and toxic volatile organic compounds (VOCs) (Spokas et al., 2011). Plants uptake N mostly in the form of $NO_3^-$ -N rather than $NH_4^+$-N and applied $NH_4^+$-N will rapidly be transformed to $NO_3^-$ -N by nitrifying bacteria at a low pH (3.5-4.5) (Hayatsu & Kosuge, 1993) which can rapidly leach through soil. The addition of biochar ash increased N mineralization rate and nitrification in most of the soils (Khanna et al., 1994). Biochar can also immobilise N (making it unavailable for plant uptake), which is essential for plant growth. Overall biochar incorporation improves the soil physical properties (low density, water, nutrient holding capacity and increased microbial activity), which can enhance plant growth.

Most research investigating the effects of biochar on crop yield was conducted in tropical climates e.g. in a field trial, maize crop yield and nutrient uptake were significantly increased with biochar incorporation in Colombia (Major et al., 2010), and in Hawaii a greenhouse trial conducted with short term crops (lettuce and corn) showed significant growth of plant biomass with biochar incorporation (Deenik et al., 2010). Ogawa and Okimori (2010) showed that various charcoals (mainly rice husk charcoal and some woody chars) improved the growth of agricultural crops (e.g. legumes) and rehabilitation of forest trees.

There have been few studies in temperate countries showing growth benefits with biochar addition. In New Zealand, Gartler et al. (2013) demonstrated that mixing biosolids with biochar had a beneficial effect on vegetable growth, whereas biochar alone had either no positive effect or a negative effect on growth. (Gartler et al., 2013). In Montana, USA perennial grass (*Koeleria macrantha*) grown in soil amended with laboratory-prepared biochar showed reduction in yield, however, biochar formed by a wildfire increased the biomass (Gundale & DeLuca, 2007). Biochar incorporated into Italian vineyard soil enhanced the water holding capacity (Baronti et al., 2014).

#### 7.3.2.3 Biomass and N uptake from the NV lignite incorporation

Figure 7-8 and Figure 7-9 show NV lignite incorporation (at all rates of application) in unlimed soil (pH 5 treatments) reduced ryegrass growth yield. In comparison, applying biosolids increased the yield of ryegrass ($p<0.05$). However, lignite + biosolids treatments decreased biomass with increased lignite rates of application from both harvests compared to the biosolids alone treatment. In the first harvest (pH 5 treatments), the addition of lignite to biosolids decreased ryegrass biomass yield by 4.7 %, 12.5 % and 18.5 % with respect to increased lignite additions (rates). From the first harvest, N uptake showed no significant difference from lignite incorporation with biosolids compared to biosolids alone. However, the 2$^{nd}$ harvest showed a significant ($p<0.05$) decrease in biomass in lignite+biosolids compared to biosolids alone. Results were similar from the second harvest (biomass reduced by 20 %).

However, the lignite+biosolids showed significantly increased N uptake from both first and second harvest compared to the control. Total biomass yield from both harvests from the lignite additions shown in Table 7.8.

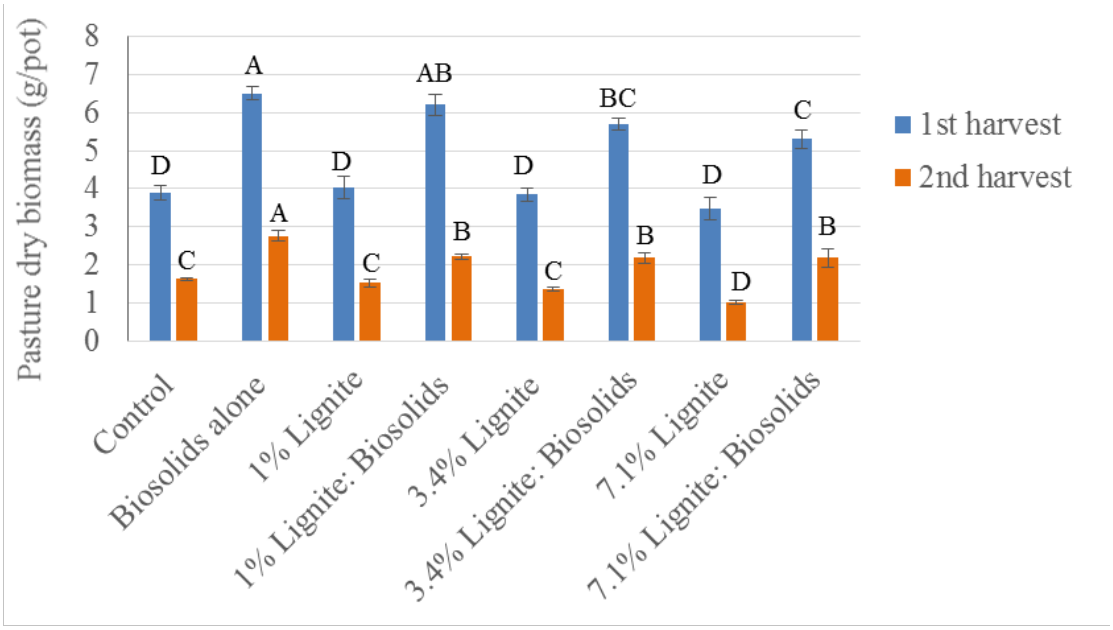


Figure 7-8. Ryegrass DM produced at two individual harvests in Pallic soil following incorporation of either biosolids or lignite at the 1st harvest and 2nd harvest where soil amendment maintained at pH 5. Values are means (n=5) with error bar ± 5 standard error of the means. Letters are according to Fisher's method (confidence level 95%).

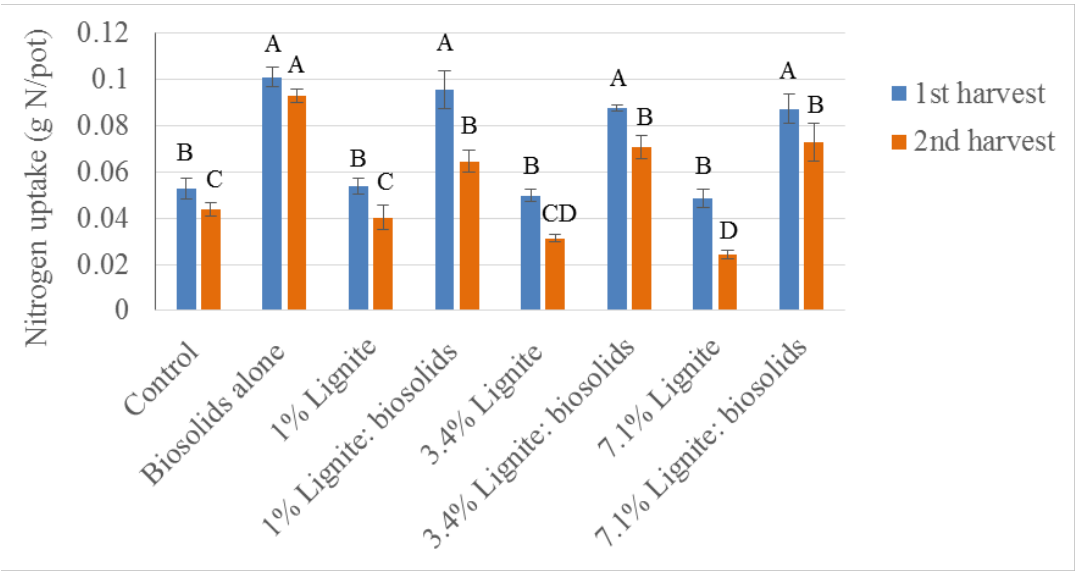


Figure 7-9. Nitrogen uptake at two individual harvests at the 1st harvest and 2nd harvest, growing mixture maintained at pH 5. Values are means (n=5) with error bar ± 5 standard error of the means. Letters are according to Fisher's method (confidence level 95%).

Table 7.8. Total biomass yield from each treatment pot.

| | **Total ryegrass dry biomass from all 3 harvests (g/pot), pH 5** | **Total ryegrass dry biomass from all 3 harvests (g/pot), pH 7** |
|---|---|---|
| Control soil | 11 (0.5)$^{d}$ | 12.1 (0.5)$^{d}$ |
| Biosolids alone | 19 (0.5)$^{a}$ | 17.1 (0.3)$^{a}$ |
| 1% lignite alone | 11 (0.7)$^{d}$ | 12 (0.6)$^{d}$ |
| 1% lignite+ biosolids | 17 (0.6)$^{b}$ | 16.3 (0.5)$^{ab}$ |
| 3.4% lignite | 10.4 (0.4)$^{de}$ | 10.5 (0.2)$^{e}$ |
| 3.4% lignite + biosolids | 15.8 (0.3)$^{bc}$ | 15 (0.5)$^{bc}$ |
| 7.1% lignite | 9 (0.7)$^{e}$ | 9.1 (0.5)$^{f}$ |
| 7.1% lignite + biosolids | 15 (0.8)$^{c}$ | 14.6 (0.4)$^{c}$ |

Superscript alpha denotes the Fisher's significance method was used to analyse the statistical significance between the treatments.

Liming (pH 7) of the soil mixture showed (Figure 7-10 and Figure 7-11) no change in the trend compared to the unlimed treatments. Overall, lignite reduced both the plant biomass yield and the ryegrass N uptake. At first harvest, the increasing rate of lignite addition decreased biomass by 6%, 10% and 13.6% respectively, with respect to biosolids alone treatments. However, N uptake showed no difference between the lignite + biosolids treatments compared to biosolids alone treatments. Similar trends were observed in the second harvest. The N uptake showed no significant differences between each treatment, but was significantly ($p<0.05$) increased compared to the control. The highest rate of lignite addition significantly reduced the biomass yield with respect to control and N uptake. Overall, biosolids+lignite treatments increased the biomass at all three rates of lignite application as well as with biosolids applications at the lower pH.

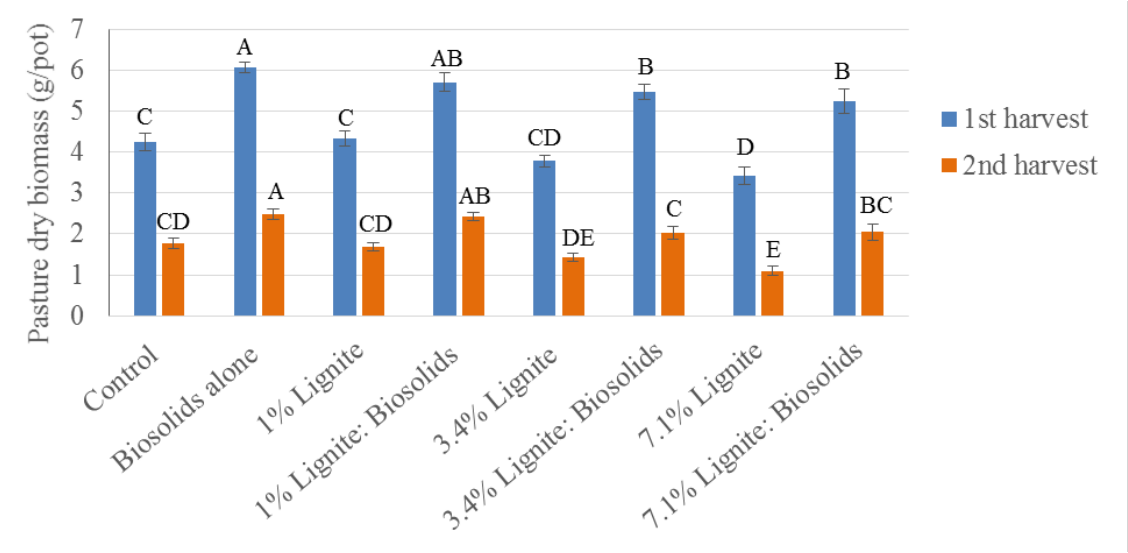


Figure 7-10. Ryegrass DM produced at two individual harvests in Pallic soil following incorporation of either biosolids or lignite at the 1st harvest and 2nd harvest where soil amendment maintained at pH 7. Values are means (n=5) with error bar ± 5 standard error of the means. Letters are according to Fisher's method (confidence level 95%).

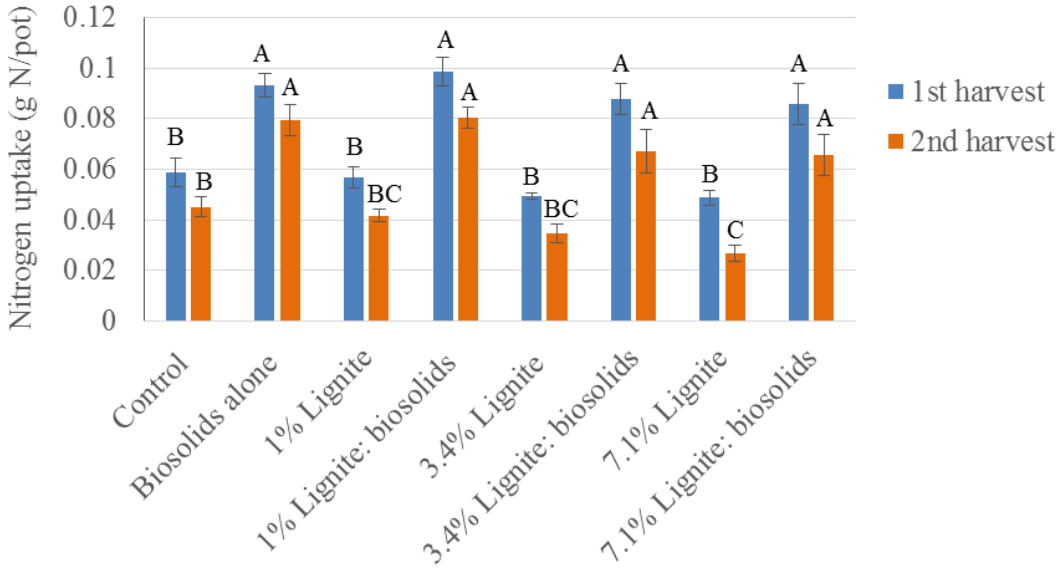


Figure 7-11. Nitrogen uptake at two individual harvests at the 1st harvest and 2nd harvest, growing mixture maintained at pH 7. Values are means (n=5) with error bar ± 5 standard error of the means. Letters are according to Fisher's method (confidence level 95%).

Pusz (2007) studied two soil types contaminated with Cu, Pb, Zn and Cd. Incorporation of lignite increased ryegrass growth (and growth increased with lignite rate, ranging between 30 – 105 t/ha), the pH of the soils was in the range of 7.2 - 7.6. This showed the acidic nature of lignite could reduce the soil's pH, which would be suitable for ryegrass growth. From this current study, Immature Pallic soil has a pH of 5.1, lignite incorporation further reducing the

pH which may not be suitable for our ryegrass growth. However, the second set of experiments where pH was maintained at 7 showed a similar pattern, with unexpected results with lignite incorporation. Richards et al. (1986) stated that even though lignite increased the total water supply, it did not increase the water available for plant use. However, lignite, probably due to its high cation exchange capacity, increased the growth of tomato (*Lycopersicon esculentum* Mill.) and a couple of indoor plants (*Boronia heterophylla* F. Muell. and *Peperomia hederifolia* Hort.).

There was a 33% reduction in biomass when sawdust was combined with biosolids, compared to the biosolids alone treatment. Biochar alone treatments showed a 16.6% decrease in ryegrass biomass yield. However, biochar combined with biosolids significantly increased ryegrass biomass yield (153%) compared to the control. At the same time, there was no significant increase with lignite+biosolids incorporated soil maintained at pH 5 and pH 7 compared to biosolids alone treatments. However, the results in Chapters 5 and 6 indicate that mixing carbonaceous amendments can reduce N mobility in biosolids. Sawdust especially, almost eliminated the $NH_4$-N leaching and reduced $NO_3$-N leaching by >40% from column leaching experiments (details in Chapter 5). The N immobilization (materials may also immobilize other growth essential macro and micro nutrients) could restrict the ryegrass growth.

### 7.3.3 Conclusion

Sawdust combined with biosolids eliminated or mitigated the negative characters of sawdust as a mulching/growth medium. At the same time, sawdust immobilized plant nutrients and reduced plant growth. Biochar incorporated with biosolids can enhance biomass and N uptake by the ryegrass, however, biochar alone decreased the biomass yield, especially in acidic soil (Balmoral soil). This could be due to less fertilizing ability of the biochar used in this experiment, the level of labile C in biochar which could have caused N mineralization or that biochar adsorbed nutrients required for ryegrass growth and some toxic component that affects

growth of the ryegrass. These experiments investigated the plant growth response over three harvests. Future experiments should investigate the plant growth response over a longer period.

When the ratios of the carbonaceous material to biosolids were considered, they varied compared to ratios used in Chapters 5 and 6, where a maximum of 1:1 of biosolids: carbonaceous material was used. In the aforementioned experiments, (a) the sawdust greenhouse experiment used 2:1 biosolids: sawdust. To find out what treatment ratio these will fit in for N leaching was described in Chapter 5. Interestingly, it falls between 2-3 % $NO_3^-$-N leaching with respect to total N (66 mg N per column) applied, (b) biochar greenhouse experiment, it was 5:4 biochar:biosolids used in this study and this ratio can significantly reduce the $NH_4^+$-N (0.2% in Chapter 4 where biosolids alone leached nearly 1% with respect to applied total N), (c) in the lignite greenhouse experiment three ratios were incorporated, they were 11:3, 1:1 and 1:2 biosolids:lignite

The most promising carbonaceous amendment was biochar, over the lignite. It increased biomass production and significantly increased N uptake by ryegrass. Therefore, if biochar were used as a soil amendment with biosolids, there is higher probability for reduced N leaching.

# Chapter 8: Summarizing conclusion

## 8.1 General discussion

My aim was to determine the changes in N fluxes when biosolids were mixed with either sawdust, biochar or lignite. In New Zealand, these materials are either waste products or are available at low cost, however, this may differ in other countries. It is important that the carbonaceous material to be mixed with biosolids does not contain significant amounts of leachable N. The level of N in the materials should be low. Taking these facts into consideration, I identified the following carbonaceous materials for my research.

**Pine wood-waste** - is waste from the timber industry, which is abundant throughout New Zealand with 190 000 $m^3$ produced per annum (FAO, 2000). It is available throughout the year at little or no cost. It does, however, cost to transport wood-waste, either from the logging site or sawmill, and sawdust is bulky and difficult to transport. It is paramount that any wood waste to be mixed with biosolids does not contain traces of timber treatments such as CCA (Copper Chromium and Arsenic). These are toxic to soil microbes as well as humans and can accumulate in the soil. Therefore, the waste timber has to be untreated. For a significant reduction in N leaching, either a minimum 1:1 ratio of sawdust to biosolids, or partly pyrolyzed biochar mixed with biosolids at 1:1 ratio, should be used .

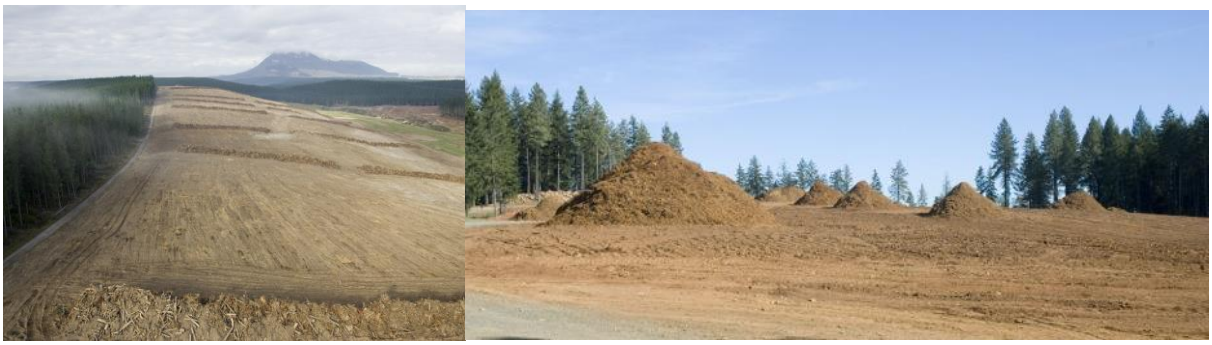

Figure 8-1. *Left:* Degraded pine land (by Brett Robinson), *Right*: Wood-waste/sawdust accumulated onsite (http://sodacanyonroad.org/forum.php?t=162&s=projectname).

My research showed that the moisture content of the sawdust profoundly affected its ability to reduce $NO_3^-$ leaching from biosolids. Dry sawdust was far superior to wet sawdust material in reducing both $NH_4^+$-N and $NO_3^-$-N leaching in column experiments (physical sorption of by sawdust). Drying sawdust could be expensive unless it occurs naturally over the warmer months. My research also showed that partially pyrolyzed sawdust may be a more cost-effective material because drying would occur during the pyrolysis process. The unpyrolyzed or low temperature-partially pyrolyzed material would then sorb $NH_4^+$ and $NO_3^-$ (Chapter 5), while the pyrolyzed fraction would persist in the soil (Chapter 3, Section:3.2.2.3.2b) and sorb increasing amounts of $NH_4^+$ as it weathers (Chapter 3, Section:3.2.2.4). In Chapter 5, I demonstrated that the most promising sawdust type was dried sawdust, bulk biochar 350$^o$C, and two low temperature biochars.

Figure 8-1 shows degraded pine forest soil and mounds of wood-waste/sawdust on the pine-harvested land. These could be reapplied to the same land, as part of rebuilding the soil, where logging occurred. This rehabilitation process could be carried out before application of biosolids, or preferably mixed with biosolids. Biosolids can be applied either to the soil surface (Figure 8-2) or mixed/ploughed in with soil (Figure 8-3). Spreading the sawdust during spring would allow it to dry, and in late summer when the sawdust is dried, biosolids could be applied on top of, or mixed together.

Figure 8-2. Solid-state biowaste applied to soil by spreading mechanism (USGS, 2015).

Figure 8-3. Solid state biowastes were incorporated (ploughing) with soil (MBI, 2015).

The layering of sawdust, and/or biochar with biosolids could be kept as a possible inexpensive management practice, as ploughing costs money. Biowaste could be applied in liquid form, either via irrigation or infused in soil (Figure 8-4)

Figure 8-4. *Left:* Liquid biowaste infused in soil, *Right*: applied along with irrigation (MBI, 2015).

**Biochar-** Compared to untreated wood-waste, biochar is relatively expensive to manufacture and transport (Chapter 1, Section 1.3). Large-scale pyrolyzation of biochar may be more cost effective compared to small-scale operations (~up to 10kg). Wang et al., (2009) propounded that pyrolysis should be a precision operation to create chars with specific properties, such as sorption of gases, $NH_4^+$ , or $NO_3^-$ (Kameyama et al., 2012). Therefore, biochars must be pyrolyzed to a degree of precision for a particular requirement. Is it possible in cheap large scale pyrolyzation?

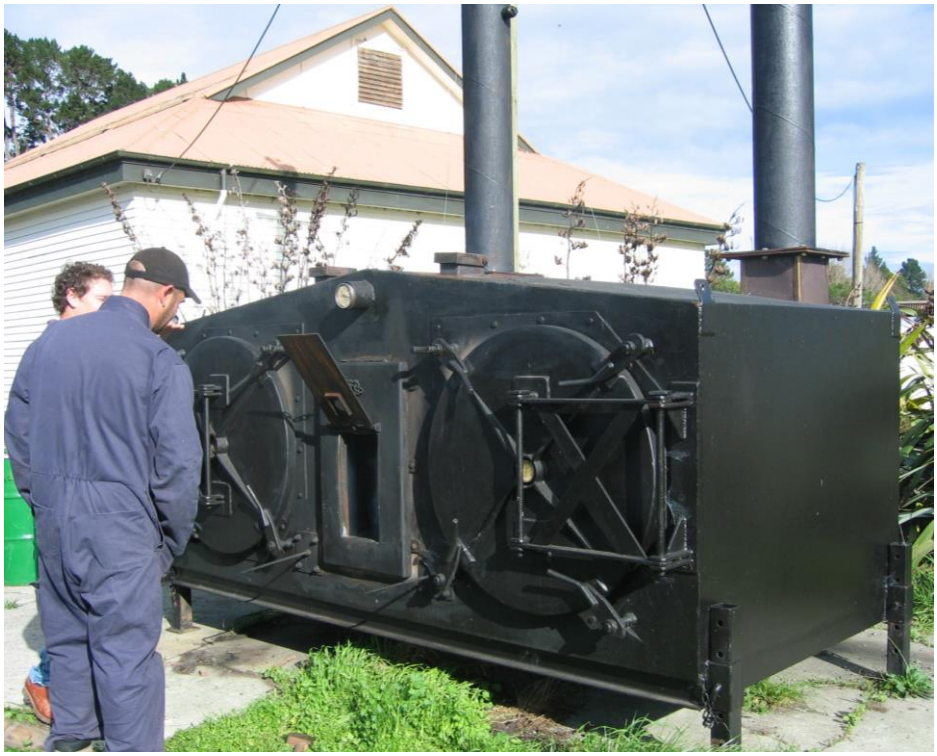

Figure 8-5. The pyrolyzer at Palmerston North belongs to the New Zealand Biochar Research Centre (When I visited this site in 2011 it was being installed, photo by Dharini on the 10/04/2011).

Currently in New Zealand, moderate scale-biochar kilns are available such as the 100 kg kiln shown in Figure 8-5. This pyrolyzer belongs to the New Zealand Biochar Research Centre, Massey University, in Palmerston North. At present, New Zealand does not have the infrastructure to produce partially pyrolyzed sawdust biochar to mix with biosolids. Assuming a biosolids: biochar ratio of 1:1, New Zealand would require 350,000 t of biochar to be produced annually. The "Carbon Scape" New Zealand produces is 550,000 t/year activated granular C (CarbonScape, 2015).

My investigations also indicated that "low-tech" biochar pyrolyzed at low temperature, containing a mixture of pyrolyzed and unpyrolyzed wood-waste may be the most effective (Chapter 4) in mitigating N leaching from biosolids. Previous studies also showed the role of low temperature biochars and their behaviour, such examples are, reduction in $NO_3^-$-N leaching by pine 350ºC (Knowles et al., 2011), low temperature (350ºC) pine (*Pinus radiata*) biochar adsorbs $NH_3$ generated from the ruminant urine-N (Taghizadeh-Toosi et al., 2012b), and biofortified vegetables grown with incorporation of 350ºC biochar and biosolids (Gartler et al., 2013).

Low-tech biochar can be pyrolyzed at the site where feedstock is readily available by using portable pyrolyzers. Munkhbat et al. (2012) used a low tech pyrolyzation system, consisting of a portable 200 L barrel, to produce biochar from wood-waste (Figure 8-6) and promoted their findings to small scale farmers and shareholders.

Figure 8-6. *Left*: Oil barrel pyrolyzer components, *Right:* fully assembled pyrolyzer (Munkhbat et al., 2012).

According to McLaughlin et al. (2012) lower temperature biochars had unusual properties that may be attributed to the higher levels of residual bio-oils and volatile matter, such biochars with lower levels of non-graphitic carbon showed a better response in most analytical testing methods, such as batch sorption to remove contaminants. The "bulk biochar" from the current study (volatile matter 53%) has potential to mitigate $NO_3^-$-N leaching from

biosolids and also has partially pyrolyzed dried woody material which was not present in other high temperature biochars specially pyrolyzed for this study.

Sorption of N by these materials is influenced by their physicochemical properties such as CEC, porosity (not measured in this current study), and surface area (not measured in this current study) for sorption (Chapter 3). Only bulk biochar and other low temperature biochars showed sorption of $NH_4^+$. There was no sorption observed by sawdust from the batch experiments (Chapter 5) even though the pine sawdust (kanuka sawdust was not tested for the sorption studies) and bulk biochar has a slightly higher CEC than the other low temperature biochars pyrolyzed using a furnace. However, the results from column leaching showed significant reduction for both $NH_4^+$ and $NO_3^-$ by both pine and kanuka sawdust. This could be due either to the physical retention/sorption of the ions or the N ion species could have been immobilized by the sawdust (especially completely dried sawdust, rather than the partially wet sawdust). On the other hand, bulk biochar and other biochars chemically sorbed $NH_4^+$, however, biochars were not effective in reducing $NO_3^-$ from biosolids. Cation exchange capacity was the main key parameter shown by most of the previous work done with N species sorption by biochars. Retention of $NO_3^-$ will not directly link to CEC, however, high CEC biochars will have to be able to hold $NH_4^+$, which is not readily available for nitrification.

The aforementioned materials were chosen because they are relevant and readily available in New Zealand. However, the availability of these and other materials will be different in other countries. For example, Sri Lanka has abundant coconut waste, palm kernel waste and tea waste that could be used as low-cost amendments to mix with biosolids. In Sri Lanka the main source of fuel for day to day cooking is firewood. The resulting ash & charcoal is spread under fruit trees, resulting in improved yields (Genxing et al., 2011). Ogawa and Okimori (2010) reported that in Asian countries, one of the most common materials for soil amendments was rice husk charcoal, which is made when fields are burned off (Figure 8-7)

soon after harvesting. The char is mixed into the soil by ploughing. Burning is required because composting of rice husk is difficult due its high silica content.

Figure 8-7. Charring process after the rice harvest in Asia (Gupta & Dadlani, 2012).

Figure 8-8 shows how biochars are produced in India where crop residues are used as a feedstock. Examples are wheat residue and cereal crops (rice, wheat, maize, mill) (Singh & Sidhu, 2014).

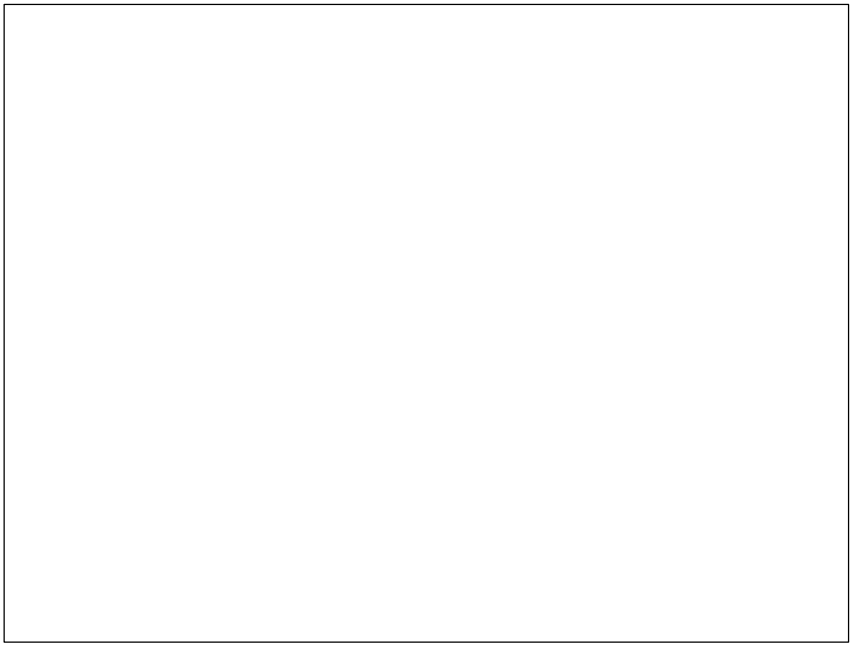

Figure 8-8. Char production in a rural part of India (Irwin, 2014).

**Lignite** is another low cost carbon-rich material. Its hypothetical structure and characteristics were given in Chapters 1 and 3. Transportation of lignite may cause health risks, due to its nature and particle size. However, there are no production issues with lignite (fossil

source of C) because of its natural occurrence. Solid Energy NZ produce 4 million t/year (Solid Energy, 2015). The production issues (manufacturing) and homogeneity within the material would not be an issue for lignite. In the future, more lignite related research work could be carried out in relation to N. It will help to determine the fate and stability of lignite and its ability to interfere with the N cycle (Chapter 3). Results from this study showed that lignite was unable to reduce N leaching from aged biosolids, with no significant reduction in either $NO_3^-$ or $NH_4^+$, in stark contrast to biochar and sawdust. It was proven that it has no efficiency in mitigating $N_2O$ emission and at the same time, it increased levels of $N_2O$ emission.

Plant growth was hindered with the incorporation of lignite (Simmler et al., 2013), however, Richards et al. (1986) and Pusz (2007) showed a positive impact on plant growth with lignite addition to soil. My research showed that the ryegrass biomass yield increased with biosolids alone and when incorporated with lignite (Chapter 6).

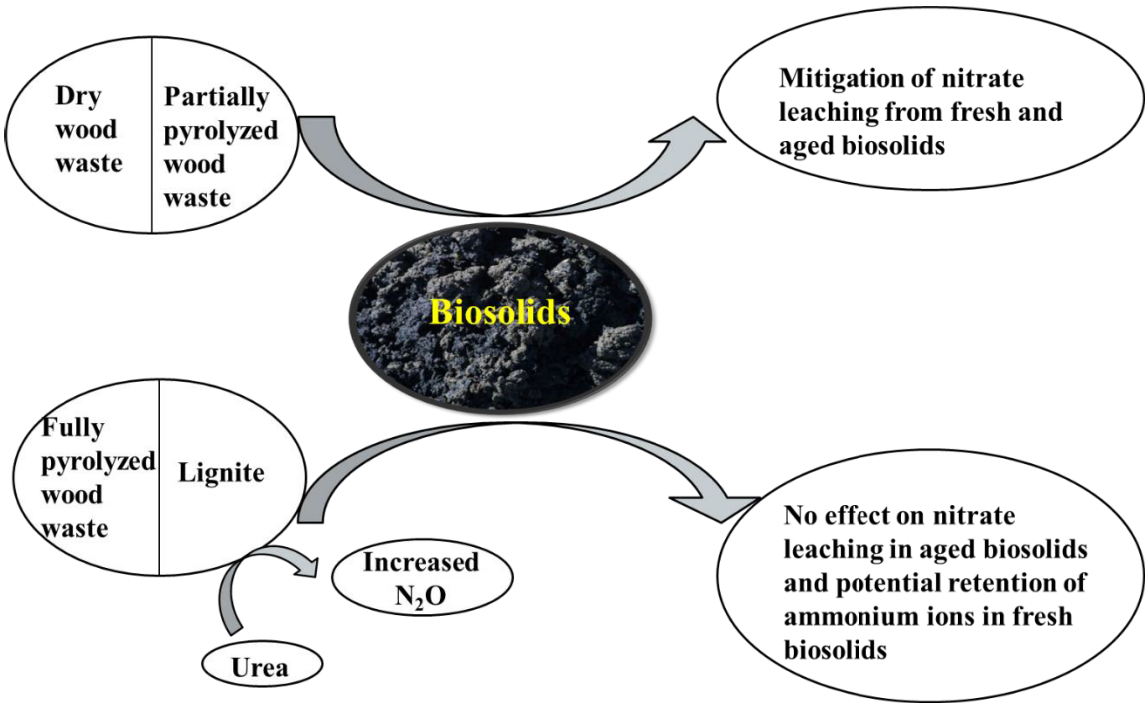


Figure 8-9 Schematic summary diagram of this current study.

## 8.2 Conclusions

Sawdust, which is abundantly available in NZ, significantly reduces $NO_3^-$ leaching from biosolids while still permitting acceptable plant growth. The effectiveness of sawdust in this

role depends on its moisture content. Sawdust could be partially pyrolyzed to reduce its moisture content. Mixtures of dried sawdust and biochar could provide a low-cost means of reusing two waste materials to rebuild degraded soils. Further research could elucidate the behaviour of other sawdust at various moisture contents.

My research indicates that carbonaceous amendments are likely to be more effective when mixed with fresh biosolids, which have a higher $NH_4^+$: $NO_3^-$ ratio compared to aged biosolids because the $NH_4^+$ will be immobilized by the high CEC of the materials. However, New Zealand's wood-waste/sawdust (mentioned in the "Discussion" above) could be beneficially mixed with biosolids to rebuild former pine-forest soils while significantly minimizing $NO_3^-$ leaching from biosolids (used in this current study). Using material on-site is advantageous because there is no transport cost. Potentially, this sawdust could be sun-dried to mitigate N leaching from biosolids. However, biochars which are partially pyrolyzed at low temperatures present another potential material to mitigate N leaching from biosolids. Again, biochar could be prepared on site using the sawdust. Lignite showed the least impact on N retention or mitigating N leaching from the biosolids. Lignite addition to soil (Chapter 6) showed increased $N_2O$ emissions and reduced pasture growth and nutrient uptake. Lignite is ineffective in reducing N mobility in soils and biosolids-amended soil.

This research outcome could lead to councils and regions collaboratively working to change use waste products as assets in order to rebuild degraded land.

## 8.3 Fertile areas for further research

Both fresh and aged biosolids could be tried at the same time in similar laboratory and field experiments. The results could reveal differences and will give more details of the N dynamics in different biosolids.

A long term (for 3-5 years with an annual application of biosolids) experiment could be conducted with multiple biosolids/carbonaceous treatments to a degraded land to monitor the effect. This experiment be can designed with a lysimeter field experiment.

Fresh and weathered biochar could be used in the above mentioned experiments. Both biochar types should be characterized and the extent of N retention analyzed. Biochars could be pyrolyzed from different kinds of feedstock, including non-woody materials as well e.g. corn stover, grass.

Lignite is a very new pathway in scientific research except for fuel or metal retention. Therefore, numerous experiments could be carried out to determine N retention. Characterize different types and compare with a reference kind of lignite if possible.

Characterize fresh and weathered sawdust and its ability to retain N. Different kinds of sawdust materials can be included for this purpose.

The effect of these amendments on soil biology could be investigated.

# Appendix A

Figure A. 1. *Left*- End-over-end shaker; *Right*- Sorption samples ready for a timely sub-sampling

Figure A. 2. Column leaching experiment in the laboratory.

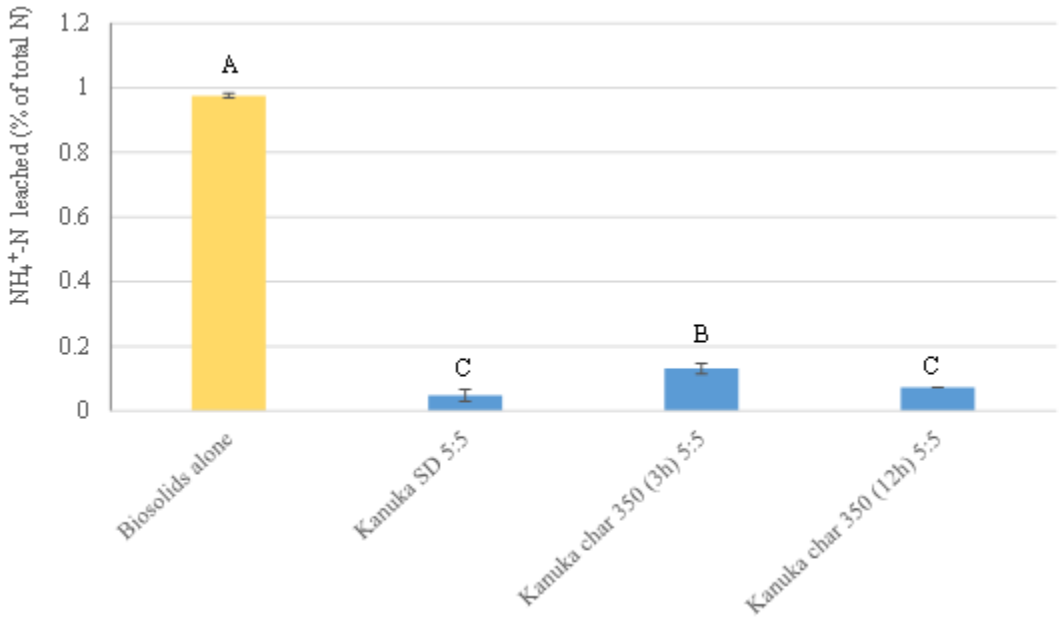


Figure A. 3. $NH_4^+$-N leached (as a % of total N in the columns), from kanuka sawdust and char columns with the biosolids. Number ratios indicate the mass of material (g): mass of biosolids (g). Bars represent the standard error of the mean (n=3).

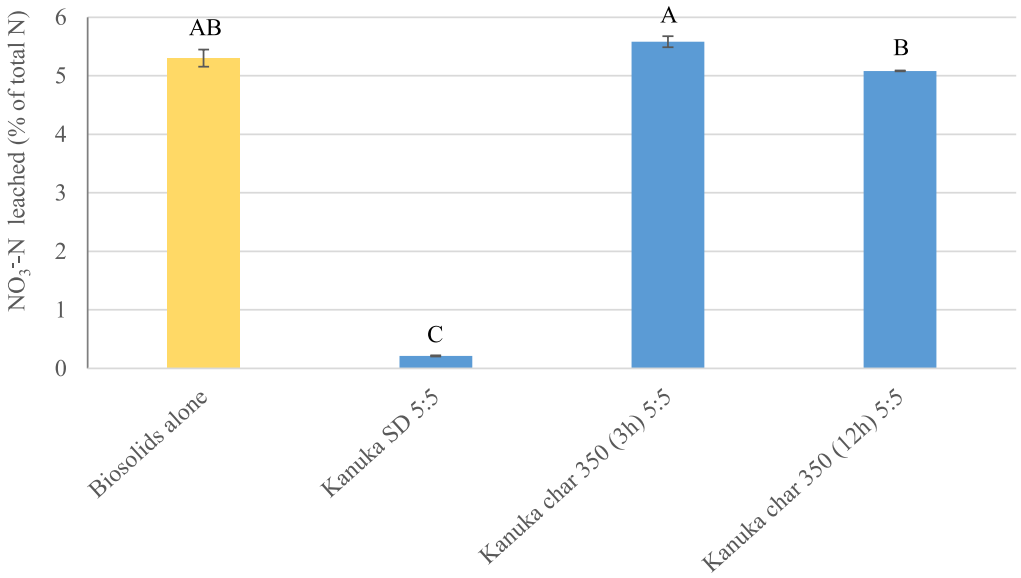


Figure A. 4. $NO_3^-$-N leached (as a % of total N in the columns), from columns with the biosolids. Number ratios indicate the mass of material (g): mass of biosolids (g). Bars represent the standard error of the mean (n=3).

Table S 1 Total elemental analysis of biochars by acid digestion, values are in mg/kg (Enders et al., 2012)

| | HTTs (°C) | Na | K | Ca | Mg | S | P | Fe | Mn | Zn | Si |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Pine | 350 | 134 | 387 | 1940 | 389 | 48 | 49 | 40 | 131 | 21 | n/d |
| | 400 | 351 | 373 | 2247 | 482 | 103 | 35 | 1166 | 258 | 66 | 10 |
| | 550 | 232 | 734 | 2255 | 707 | 237 | n/d | 110 | 298 | 38 | n/d |
| Corn stover | 500 | 1384 | 24817 | 11699 | 9510 | 739 | 1852 | 1063 | 199 | 72 | 241 |
| | 550 | 778 | 23929 | 9804 | 8891 | 731 | 2093 | 845 | 208 | 82 | 335 |
| | 600 | 1539 | 24616 | 9383 | 8582 | 801 | 2114 | 1362 | 226 | 70 | 322 |
| Oak | 400 | 321 | 1462 | 1061 | 61 | 86 | 5 | 169 | 15 | 33 | 4 |
| | 600 | 52 | 2061 | 1210 | 100 | 137 | n/d | 158 | 23 | 23 | n/d |

HTTs : Highest Treatment Temperatures: n/d –not detected

Table S 2 Influence of pyrolysis temperature on water-extractable major cations, values are in mg/kg (Kloss et al., 2012)

| | HTTs | Na | K | Ca | Mg |
|---|---|---|---|---|---|
| Wheat straw | 400 | 15 (1) | 10200 (900) | 242(37) | 89 (8) |
| | 460 | 13 (3) | 13500 (900) | 709 (236) | 212 (18) |
| | 525 | 20 (3) | 18200 (1900) | 187 (32) | 36 (1) |
| Spruce wood & leaf mix | 400 | 15 (1) | 1200 (130) | 455 (37) | 112 (10) |
| | 460 | 10 (1) | 1300 (200) | 360 (8) | 29 (3) |
| | 525 | 10 (2) | 1600 (90) | 178 (9) | 34 (1) |
| Poplar wood | 400 | 6 (1) | 2500 (60) | 1100 (180) | 246 (23) |
| | 460 | 6(1) | 2500 (40) | 437 (26) | 101 (17) |
| | 525 | 9(3) | 1700 (90) | 232 (118) | 40 (8) |

HTTs : Highest Treatment Temperatures

# Appendix B

Figure B. 1. Left – Digging the monolith at the sheep farm; Right- transferred to the trench at the Field service centre at the University premises.

Figure B. 2. *Left – Right:* Lifting frame attached with the lysimeters to invert upside down; preparation to install drainage system; placed in the trench, before the surrounding filled with soil.


Figure B. 3. Lysimeter trench location at Lincoln University (source: Google Earth)

Figure B. 4. *Left- Right:* Top 10 cm lysimter soil was removed; mixed with treatment and placed back in the lysimeter with the help of my supervisor Brett Robinson; each lysimeter was equipped with the irrigation system.

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# Glossary

AgTU – Silver Thiourea
AOB - Ammonia oxidising bacteria
As - Arsenic
B - Boron
BET - Brunauer, Emmett and Teller
Ca - Calcium
CCA - Copper Chromium and Arsenic
Cd – Cadmium
CFU – Colony forming units
$CH_4$ – Methane
$CO(NH_2)_2$ – Urea
Cr- Chromium
Cu - Copper
DAP – Diammonium phosphate
DDT- Dichlorodiphenyltrichloroethane
DIC - Dissolve Inorganic Carbon
DM – Dry matter
EDC - Endocrine disrupting compounds
EPA- Environmental Protection Authority
Fe - Iron
FIA - Flow Injection Analysis
GHG - Green House Gases
$H_2O_2$ – Hydrogen peroxide
$H_2S$ – Hydrogen sulphide
$H_2SO_4$ - Sulfuric acid
HA - Humic acid
HCl – Hydrochloric acid
Hg – Mercury
$HNO_3$ – Nitric acid
HTT – Highest Treatment Temperature
IC - Inorganic Carbon
ICP-OES - Inductively Coupled Plasma Optical Emission Spectrometer
IHSS- International Humic Substances Society
IPCC - Intergovernmental Panel on Climate Change
K - Potassium
KCl - Potassium chloride
KOH – Potassium hydroxide
Mg - Magnesium

Mn – Manganese
Mo - Molybdenum
N - Nitrogen
$N_2O$ – Nitrous oxide
NaOH – Sodium hydroxide
$NH_3$ - Ammonia
$NH_4^+$ - Ammonium ion
NO - Nitric oxide
$NO_2^-$ - Nitrite
$NO_3^-$ - Nitrate
NZ-NCNM - New Zealand's National Centre for Nitrous Oxide Measurement
P - Phosphorous
PAH - Poly-aromatic hydrocarbons
Pb - Lead
PBDE - Polybrominated diphenyl ethers
PCB - Polychlorinated biphenyls
PCP - Personal care products
PFU – Plaque forming units
S - Sulphur
$SO_2$ – Sulphur dioxide
TC - Total Carbon
TGA - Thermal Gravimetric Analysis
TOC - Total Organic Carbon
WestTP- Western treatment plant (Melbourne)
WSC - Water Soluble Carbon
WTP – Waste water treatment plant
Zn -Zinc
$ZnCl_2$ – Zinc chloride
Zn -Zinc